Research Paper

Controlling The Pathways To The Synthesis Of A New Lithium Manganate

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Abstract

Lithium manganate crystals are potential material for lithium-ion batteries. This project attempts to optimize the growth conditions for lithium manganate crystals in order to produce the most successful crystals. The results show that $LiMnO_2$ -- a key precursor to growing lithium manganate single crystals -- must be of the highest possible purity for high yield crystal growth. Several variables that affect the purity of $LiMnO_2$ were tested and it was found that the temperature at which the precursor is removed from a furnace as well as its growth environment strongly affect its quality. The ability to produce higher purity lithium manganate crystals could make lithium-ion batteries an even more efficient energy source, therefore reducing the human impact of climate change. This work was supported as part of GENESIS: A Next Generation Synthesis Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award Number DE-SC0019212.

Introduction

Global fossil fuel usage is the largest contributor to anthropogenic climate change. Lithium-ion batteries provide a high efficiency energy source that can replace fossil fuels and mitigate climate change. Their rechargeability, high power, and low weight make these batteries more efficient than previous energy sources. Lithium manganates are potential anode materials for such batteries. The lithium manganate crystals produced in this project were low cost and used abundant reactants like Li_2CO_3, Li_2O, MnO, and LiCl. The growth of the crystals did not require the use of expensive equipment or machinery. The ability to make cheap lithium-ion batteries is essential in order for renewable energy to become cheaper than fossil fuels.

The lithium manganate crystals have the formula Li_2MnO_3 and have a monoclinic structure.They are dark red and hexagonal. The following reactions took place in order to synthesize the lithium manganate crystals:

$$MnO + O_2 \rightarrow Mn_2O_3$$

$$Mn_2O_3 + Li_2CO_3 \rightarrow 2LiMnO_2 + CO_2$$

$$LiMnO_2 + Li_2O + LiCl \rightarrow 2Li_2MnO_3$$

Methods

Multiple experiments were carried out in order to determine the ideal growth environment for $LiMnO_2$. $LiMnO_2$ is produced by reacting Li_2O and Mn_2O_3. The first sample that was grown was $LiMnO_2$ FSC 656.

FSC656 LiMnO2

Chemical (vendor, part no., lot no.)	Target mass (g)	Actual mass (g)
Li2CO3 (Alfa 13418)	0.3188	0.31913
Mn2O3 (FSC0650)	0.6812	0.60116

The reactants were pressed into a pellet and sealed in a 10cm long quartz tube. The quartz tube was placed in a furnace at room temperature.

Temp. 1 (C):	**Time 1 (min)**:	**Temp. 2 (C)**:	**Time 2 (min)**:	**Temp. 3 (C)**:	**Time 3 (min)**:	**Temp. 4 (C)**:	**Time 4 (min)**:	**Temp. 5 (C)**:
RT	120	750	960	750	1	0	9999	520

Once the sample was taken out of the furnace, a hammer was used to shatter the quartz tube and take out the LiMnO2 sample. A loud “pop” was heard once the quartz tube was shattered and small droplets were visible on the quartz glass.

UV-vis and X-ray powder diffraction were both used to determine the purity of FSC 656. The X-ray diffraction confirmed that FSC 656 was highly pure and contained very little contaminants. Li2MnO3 crystals were then grown from FSC 656 LiMnO2 sample.

FSC 658 Li2MnO3

Chemical (vendor, part no., lot no.)	**Target mass (g)**	**Actual mass (g)**
LiMnO2 PC FSC0656	0.1277	0.12796
Li2O, Li metal self propagating torch fire reaction	0.0745	0.07631
LiCl Alfa 10515 113 C salt box	0.7978	0.77834

The reactants were combined and sealed in a 7cm long silver tube. The silver tube was then placed into the furnace at 200C.

Temp. 1 (C):	**Time 1 (min)**:	**Temp. 2 (C)**:	**Time 2 (min)**:	**Temp. 3 (C)**:	**Time 3 (min)**:	**Temp. 4 (C)**:	**Time 4 (min)**:	**Temp. 5 (C)**:
200	120	900	120	900	3600	600	9999	600

The Li_2MnO_3 crystals that were grown from $LiMnO_2$ FSC 656 were highly pure and x-ray diffraction analysis of the crystals confirmed them to be a new form of lithium manganate crystals.

However, the growth conditions of FSC 656 were not ideal. Removing the sample from the furnace at 520C allowed for an increased risk of the quartz tube shattering violently when broken open with the hammer. In addition, using wet Li_2CO_3 increased the vapor pressure within the quartz tube while it was in the furnace and therefore increased the risk of the tube exploding in the furnace. After the production of FSC 656, the growth conditions of $LiMnO_2$ for future samples were altered in order to make it more safe.

In a second attempt to grow Li_2MnO_3 crystals, the $LiMnO_2$ sample that was used (FSC 667) was taken out at room temperature and used dried Li_2CO_3 as a safety precaution. CaO was also added to the sample to remove CO_2 gas from the quartz tube to further prevent the tube from exploding in the furnace. However, the sample was not pure and the crystals that were grown from it were not successful. Therefore, it was concluded that the higher the purity of $LiMnO_2$, the more successful the Li_2MnO_3 crystal growth.

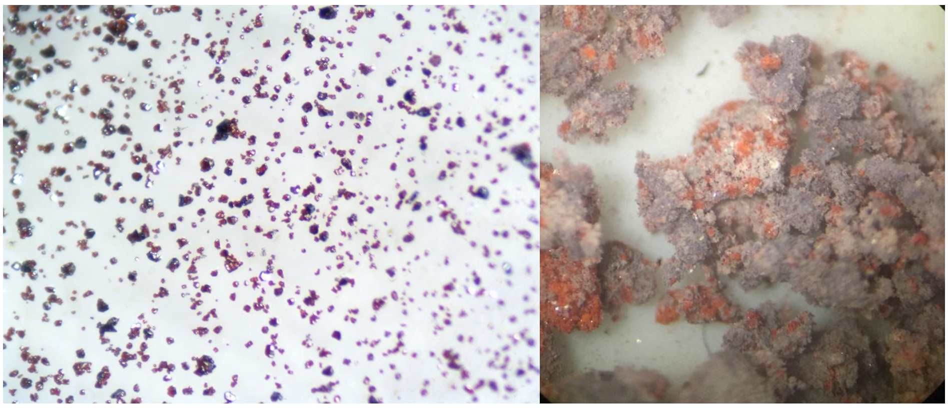


Figure 1. Li_2MnO_3 crystals grown from FSC 656-- high purity $LiMnO_2$ (left) Li_2MnO_3 crystals grown from FSC 667-- lower purity $LiMnO_2$ (right)

The first experiment was to test the effect of using dry reactants on the purity of the LiMnO2 sample. Li2CO3 is hygroscopic and attracts water into the LiMnO2 sample and this might have an effect on the purity. Two LiMnO2 samples were prepared: FSC 758 and FSC 1051. Both samples were grown under the exact sample conditions however the Li2CO3 in FSC 758 was placed in a furnace at 200C before being mixed with the other reactants in order to remove the water. UV-vis and X-ray powder diffraction were both used to determine the purity of the LiMnO2 samples. Li2MnO3 crystals were then grown from FSC 758 and FSC 1051 and these crystals were compared to the crystals grown from FSC 656.

The second experiment was to determine whether the temperature sample is taken out of the furnace has an effect on the purity. LiMnO2 samples FSC 759 and FSC 1096 were grown under the exact same conditions as FSC 656 however FSC 759 was taken out of the furnace at room temperature instead of at 520C like 656 and 1091 was taken out at 700C. X-ray diffraction and UV-vis were used to compare the purity of FSC 759 and FSC 1096 to FSC 656.

Results

It was found that LiMnO2 sample FSC-656 had the highest purity compared to all of the other LiMnO2 samples and it was the only sample that successfully grew Li2MnO3 crystals. When the quartz tube was cracked open to retrieve the sample, there was a loud popping sound and small droplets were found on the walls of the quartz tube. When determining the purity of future LiMnO2 samples, their purities were compared to that of FSC 656.

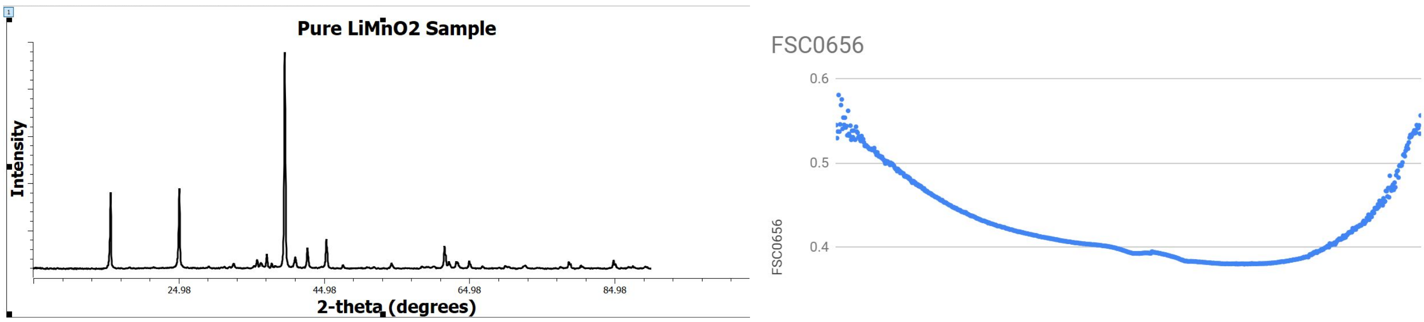
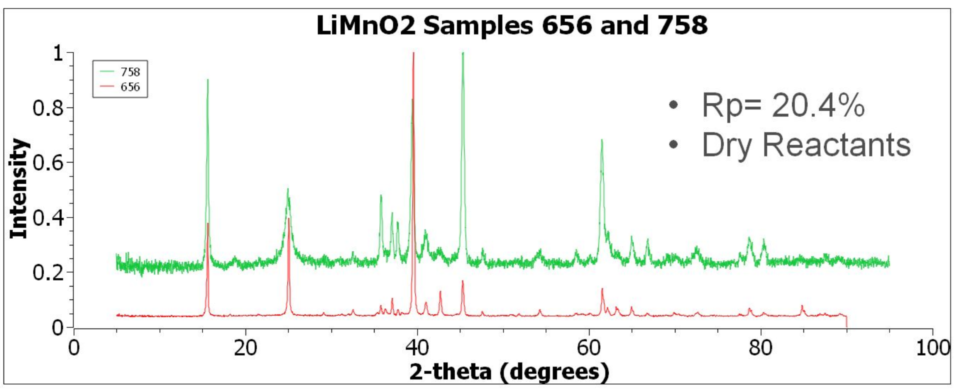
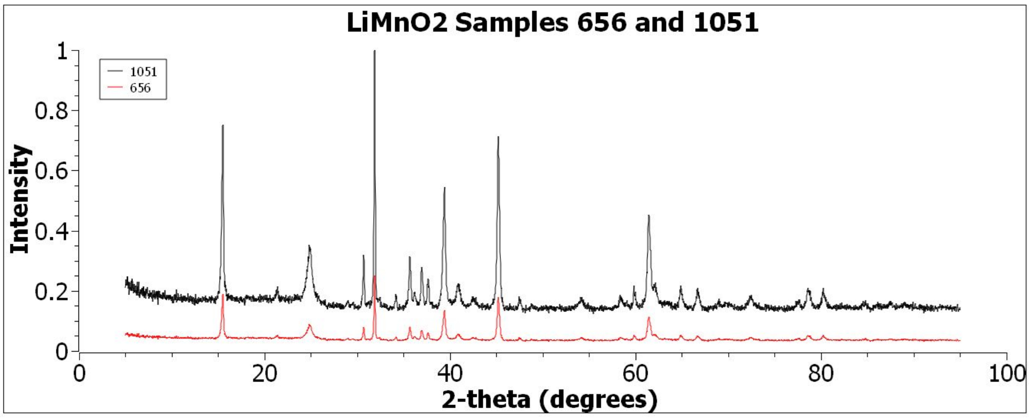


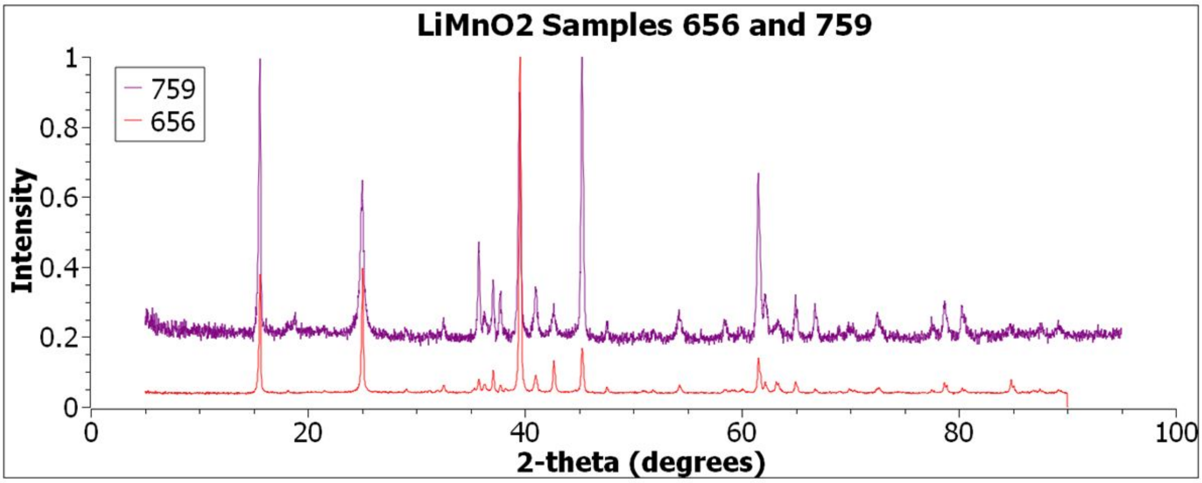
Figure 2. X-ray powder diffraction graph for FSC 656 LiMnO2 (left) UV-vis graph for FSC 656 LiMnO2 (right)

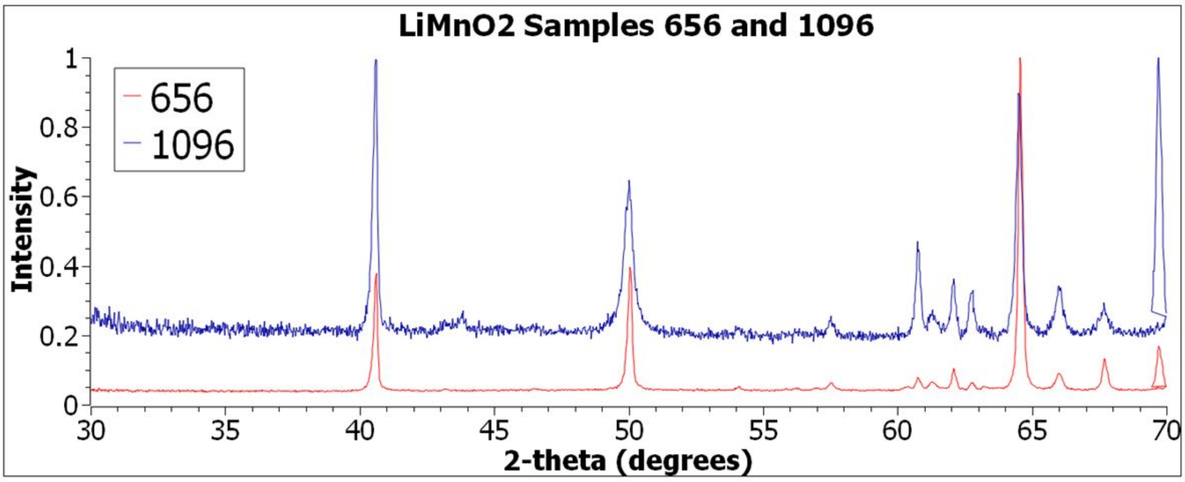
The first experiment was to determine whether using dried reactants had an effect on the purity of LiMnO2. The X-ray powder diffraction graphs for FSC 758 and FSC 1051 were compared to FSC 656 to determine the purity. LiMnO2 sample 1051 had a smaller percent difference with the FSC 656 graph. Therefore, it was concluded that using wet Li2CO3 is ideal in order to have higher purity LiMnO2. Even though FSC 1051 was of a higher purity than FSC 758, it still did not grow successful crystals.





The second experiment was to determine whether the temperature the sample was taken out of the furnace. FSC 656 was taken out at 520C, FSC 759 was taken out at room temperature, and FSC 1096 was taken out at 700C. Neither samples FSC 759 or FSC 1096 grew successful crystals. The X-ray powder diffraction graph for FSC 1096 more closely resembled the graph for FSC 656 however it was still not of a high purity.





Conclusion

Having LiMnO2 in high purity yields the most successful lithium manganate crystals. Using wet Li2CO3 led to a higher purity LiMnO2 sample than the dried Li2CO3 however it did not yield successful crystals. The excess water in the sample might have reacted with an impurity thus producing a LiMnO2 sample of a higher purity. The samples FSC 759 and FSC 1096 were taken out of the furnace at room temperature and 700C respectively and did not produce successful crystals. The only successful lithium manganate crystals were grown from LiMnO2 FSC 656 which was taken out at 520C. Lithium carbonate has a temperature range at which it dissociates and this might be related to the temperature range required to yield highly pure LiMnO2. More experiments would need to be done to determine what the ideal final temperature of a LiMnO2 sample is in order for it to be highly pure and to determine which other growth conditions affect the purity of LiMnO2.

Bibliography