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Estimating the cost and energy demand of producing lithium manganese oxide for Li-ion batteries

Chemical Sciences and Engineering Division

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prepared by Naresh Susarla and Shabbir Ahmed Chemical Sciences and Engineering Division, Argonne National Laboratory

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Abstract

Lithium Manganese Oxide (LMO) is one of the important cathode active materials used in lithium ion batteries of several electric vehicles. In this paper, the production of LMO cathode material for use in lithium-ion batteries is studied. Spreadsheet-based process models have been set up to estimate and analyze the factors affecting the cost of manufacturing, the energy demand, and the environmental impact. Two processes based on the solid-state synthesis method and a sol-gel method have been explored. Results show that the solidstate process is more cost-effective because of its lower cost of raw materials. The production cost for a solid-state process is \$7 kg⁻¹ and requires 6 kWh·kg⁻¹ of energy. The pack level cost of electric vehicle battery using LMO as a primary active material is studied as a function of LMO production cost and other parameters. The potential for reducing the cost of automotive batteries to \$100 per kWh is explored in terms of LMO price and plant production volume (economy of scale), using Argonne's BatPaC spreadsheet tool.

Keywords

Lithium manganese oxide, Li-ion battery, cathode manufacturing, process model, technoeconomic analysis

Highlights

- Techno-economic analysis of LiMn₂O₄ production for use in battery cathodes
- Solid-state process is cheaper but more energy intensive than sol-gel process
- The production cost for solid-state process is \$7 kg⁻¹ at a capacity of 60 MT day⁻¹
- Cost of purchased materials contribute nearly 64% of the total production cost
- Strategies are explored to achieve USDOE cost target of \$100 kWh⁻¹ using LiMn₂O₄

Abbreviations

LMO	Lithium manganese oxide
EMD	Electrolytic manganese dioxide
DOE	U.S. Department of Energy
GHG	greenhouse gas
CEPCI	Chemical Engineering Plant Cost Index
GWh	Giga-watthour
NCM	Nickel Cobalt Manganese oxide
Bat100	Electric vehicle battery with capacity of 100 kWh and power of 300 kW $$

1. Introduction

Lithium-ion batteries are now commonly used in electric and hybrid electric vehicles. The performance and cost of these batteries will greatly influence the market penetration of electric vehicles. The U.S. Department of Energy (USDOE) is driving multiple programs [1] to reduce the cost of automotive batteries below \$100 kWh⁻¹. Results generated from a battery cost modeling tool, BatPaC [2], developed by Argonne National Laboratory indicates that the purchase cost of the cathode active material contributes more than 20% to the cost of the battery pack.

Notwithstanding its low capacity, the spinel-type LiMn₂O₄ (LMO) is a valued cathode active material because of its low cost, high charge and discharge rate capability, low toxicity, and the abundance of Mn. It has been used in the batteries of several electric vehicles, either by itself or blended with other cathode active materials.

In this work, the cost and energy required for producing spinel-type lithium manganese oxide (LiMn₂O₄) or LMO for use as a cathode active material is studied. A comprehensive review of existing processes for producing LMO is presented and classified into 4 categories based on production technique. The pros and cons of these approaches are discussed and 2 plausible processes are selected for a techno-economic analysis based on their suitability for large scale production. The primary contribution of this article stems from the urgent need to reduce the cost of batteries. This work presents a model-based framework to estimate the cost of lithium-ion battery materials using an example of a LMO-based cathode material. The framework is essential in understanding and analyzing the effects of engineering choices (plant capacity, process selection, material choices, etc.) and process parameters during material production on the overall battery cost. To accomplish this an analysis of the various design, operational, and economic factors is presented to

understand their effects on the production cost and energy demand. A cost focused sensitivity analysis is presented to study and develop strategies for achieving the pack-level battery cost target of \$100 kWh⁻¹ for batteries using either LMO or blended positive electrodes. Finally, the cost of a battery pack is evaluated as a function of the LMO production cost and the capacity of the battery manufacturing facility.

2. Synthesis of lithium manganese oxide: a literature review

Thackeray and Rossouw[3] proposed a solid state approach to produce spinel phase $LiMn_2O_4$ by reacting lithium and manganese carbonates (i.e. Li_2CO_3 and $MnCO_3$) at ~600 °C. Tang et al.[4] suggested to mix a 38 wt. % solution of Mn(NO₃)₂ with LiCl such that the weight ratio of Mn(NO₃)₂ to LiCl is 0.08. The mixture is first dried at 120 °C to obtain a uniformly mixed powder of Li and Mn sources, then heated in an electric furnace to 650-950 °C, and finally cooled slowly to obtain LiMn₂O₄. Eberman et al.[5] suggested using MnCO₃ and Li₂CO₃ as the starting materials. They suggested a preprocessing step involving wet milling with de-ionized water as it is significantly faster than dry milling and promotes the formation of single-phase crystals. Also, the saving in milling time offsets the time required to dry the slurry. Jo et al.[6] proposed a solid state method for preparing spinel type lithium manganese oxide material for cathodes by reacting a mixture of MnO₂ and Mn_3O_4 with Li₂CO₃ where, Mn_3O_4 was obtained from the calcination of MnO_2 for ~3 h. The mixture of oxides in 1:1 ratio is washed with a weak solution of HCl with pH of 3 to 4. The washed mixture is heated to 500 °C for 5 h. The dried oxide powder is first mixed with Li₂CO₃ such that Li:Mn in the mixture is 1:2, and then calcined at 850 °C for 24 h to form spinel-type crystals of LiMn₂O₄. Zoujun et al.[7] proposed a method for preparing spinel type LiMn₂O₄ crystals by mixing lithium and manganese salts in an aqueous solution along with acetylene black. The solution is dried at ~ 60 °C to remove the solvent and the powder

is calcined at 600-700 °C for up to 2 h. The product from calcination is washed and dried to obtain the LiMn₂O₄ crystals. In their study, Zoujun et al. [7] demonstrated their approach for using a variety of salts for lithium and manganese sources such as LiCl-Mn(NO_3)₂, LiNO₃-MnCl₂, Li₂CO₃-MnCl₂, Li₂CO₃-MnSO₄, and LiCl-MnCl₂. Wang et al.[8] proposed a solid state method for producing LiMn₂O₄ spinel material using electrolytic manganese dioxide (EMD) and lithium carbonate (Li₂CO₃) as the starting materials. Their approach involved washing EMD with H₂SO₄ and reacting it with a saturated solution of LiOH for 24 h at 22 °C to pre-lithiate EMD. The solids are filtered from the hydroxide solution and dried. The dried powder is then sintered along with Li₂CO₃ at 750 °C for 24 h. Ahn and Song[9] found that sintering LiOH and MnO₂ at 750 °C for 48h and then slowly cooling at 1 °C per minute vielded better cycling performance from the produced LiMn₂O₄. Saidi et al.[10] suggested making a solution of lithium nitrate and manganese acetate, in water such that the pH of the solution is maintained around 7 to 11. This solution is dried in a spray dryer at \sim 100-150 °C to obtain a homogenously mixed powder of the lithium and manganese compounds. which is then heated to 400 °C in an oven to produce LiMn₂O₄ crystals. Wan et al.[11] suggested reacting electrolytic MnO₂ (EMD) with small lithium metal blocks such that Li:Mn is 1:2 in the reaction mixture. The reaction mixture is slowly heated to 750 °C and then sintered for 2 h to produce LiMn₂O₄. Berbenni and Marini[12] proposed a series of methods for preparing LiMn₂O₄ through calcination of lithium carbonate with a variety of manganese compounds (i.e. Mn₃O₄, MnCO₃, and MnO) at ~700 °C. They further suggested that high energy dry milling improved the electrochemical performance of the produced LiMn₂O₄. In their optimization study, Momchilov et al.[13] and Zhang and Jow[14] identified that using LiOH and MnO₂ as starting materials and calcination at ~750 °C for \sim 20 h produced spinel type crystals of LMO with an improved electrochemical capacity

and cyclic performance. Huang et al. [15] proposed a carbohydrate assisted combustion method for the synthesis of spinel-type LMO. They used $LiNO_3$ and a 50% (w/w) aqueous $Mn(NO_3)_2$ solution in a Li/Mn atomic ratio of 1.05:2.0. The fuel used for this process was a 9:1 stoichiometric mixture of acetylacetone and sorbitol or Vitamin-C. The aqueous mixture is first dried in vacuum and then calcined at 400 °C for 4 h before sending to ball mill for grinding at high temperature. The calcined powder was further calcined at 600 °C for another 4 h to form crystalline LMO. Li et al. [16] proposed a similar high temperature grinding-based combustion synthesis method for LMO. They used a mixture of lithium acetate, manganese acetate tetrahydrate, and citric acid along with lithium hydroxide monohydrate and manganese nitrate tetrahydrate as raw materials. Hashem et al. [17] suggested using lithium and manganese acetate dissolved in distilled water with citric acid and ethylene diamine tetra-acetic acid (EDTA) as fuels for a sol-gel based synthesis of spinel-type LMO. In another sol-gel type synthesis method, Barboux et al.[18] proposed to heat an aqueous solution of lithium hydroxide (LiOH) and manganese acetate $(Mn(CH_3COO)_2)$ in ammonium hydroxide (NH_4OH) . The product of this reaction is the lithium manganese acetate precipitate, which is dried at 90 °C and then calcined at 600 °C to produce crystalline LiMn₂O₄. Dziembaj and Molenda[19] proposed a similar method, where LiNO₃ and Mn(CH₃CO₂)₂ are dissolved in deionized water and mixed with ammonia solution to form a gel. This compound is first dried, then calcined at 300 °C for 24 h, and finally cooled to the room temperature to obtain spinel phase crystals of LiMn₂O₄. Sun et al.[20] proposed another sol-gel approach using aqueous lithium and manganese acetates mixture along with aqueous poly acrylic acid. Nitric acid is added to bring the pH level to 1 -3. The reacting mixture is first heated at \sim 75 °C until a transparent gel is obtained (\sim 10h) and then calcined at 800 °C for 10 h to obtain crystalline LMO. In a different approach, Lv

et al.[21] and Chen et al.[22] suggested making LiMn₂O₄ by reacting LiOH with an aqueous solution of KMnO₄ (0.2 mol L⁻¹) and aniline (0.02 mol L⁻¹). The reaction mixture is heated to 100-180 °C for 24 h and then cooled to room temperature. The LiMn₂O₄ formed is filtered from the mixture and dried at 60 °C. Similar to this approach, Wu et al.[23] presented another hydrothermal method for preparing LiMn₂O₄ by reacting the aqueous solution of LiOH, EMD, and Mn(NO₃)₂ in an autoclave at 280 °C for 36 h. The reaction products were filtered, washed with water and air dried to obtain the spinel crystals. Jiang et al.[24] suggested reacting an aqueous solution of LiOH and MnO₂ in a Teflon coated autoclave for several days at 200 °C, followed by drying at 70 °C to obtain the crystals. Yang et al.[25] proposed a combustion based method for the synthesis of spinel phase LiMn₂O₄ where, LiNO₃ is mixed with urea (CO(NH₂)₂) and 50 wt% solution of Mn(NO₃)₂ in water. The mixture is heated to 800 °C and subsequently cooled to the room temperature to obtain spinel phase LMO. Lee et al. [26] proposed a similar method, where the reaction mixture consisting of LiOH, aqueous solution of Mn(NO₃)₂, and urea is maintained at 80 °C for several hours to produce LMO. Zhou et al. [27, 28] proposed mixing manganese carbonate (MnCO₃) and Li₂CO₃ with 10 wt.% glucose in a ball mill, followed by calcining at 500 °C for 1 h to produce LiMn₂O₄.

3. Process descriptions

As observed from aforementioned review, a variety of methods have been proposed for manufacturing LMO. However, an analysis of process, cost, and energy constraints for commercial-scale production have not been studied in the literature. Such an analysis is important to estimate the potential and understand the avenues for cost reduction and its eventual significance in reducing the cost of a battery pack. This report presents a systematic approach to fill the aforementioned gap in the literature. Synthesis methods proposed in the literature can be primarily classified into 4 categories, i.e. solid state, sol-gel, hydrothermal, and combustion method. For large-scale operations, controlling the production process is difficult when using a combustion method and typical yields for hydrothermal methods are low. For these reasons, this study considers a solid-state process (P1) and a sol-gel process (P2) to develop a process model for large-scale production of LMO. The focus of this report is to study and analyze the relative differences and similarities between the two approaches in terms of production cost and energy demand. A brief description of the two manufacturing processes (P1 and P2) is presented below. These processes are a combination of one or more similar methods described in the literature and are chosen based on the availability of process data.

3.1. Process 1 (P1): Solid-State Synthesis

The solid-state method for manufacturing LMO discussed here uses electrolytic manganese dioxide (EMD) and lithium carbonate (Li₂CO₃) as the raw materials for sourcing manganese and lithium. The process flow sheet for P1 is shown in Figure 1.

The purchased EMD is first washed with a 1M H₂SO₄ solution to remove any trace amounts of metals present. The slurry is then filtered and the solids are washed with process water in a 3-stage vacuum drum filter. Filtered H₂SO₄ solution from stage 1 is about 98% of the original amount and is sent offsite for second use/disposal. For brevity of the model, we assume a representative cost of \$0.15 kg⁻¹ for handling/disposal of spent H₂SO₄. The 2nd and 3rd stages of filtration involve washing of the cake with process water. The wet filter

cake of EMD is mixed with Li₂CO₃ powder in a ball mill for wet milling. Additional water may be used to ensure the solids content in the ball mill is around 60% by weight.



Figure 1 Process flow sheet for manufacturing LMO by a solid state process (P1) The wet milled slurry is then dried at 150 °C in a spray dryer. The obtained powder is a homogenous mixture of EMD and Li₂CO₃. This homogenous mixture powder is calcined in a furnace at 750 °C for 20 h using a saggar-based feeder system. In a saggar-based feeder system, the feed powder is distributed in multiple saggars (ceramic containers), which are then passed through a kiln on a conveyor system for the desired residence time to facilitate calcination. The following reaction between the two raw materials is promoted in the kiln.

$$Li_2CO_3 + 4MnO_2 \rightarrow 2LiMn_2O_4 + CO_2 + \frac{1}{2}O_2$$

Each saggar is assumed to hold up to 5 kg of materials and can be re-used up to 20 times. After calcination, the heated solids are cooled through a forced-convection cooling chamber at a rate of 1 °C per minute to obtain spinel-type LMO. Once, the solids attain room temperature in around 12 h, the calcined solids are milled in a dry ball mill to reduce the size of solid particles to less than 44 micrometers (-325 mesh).



3.2. Process 2 (P2): Sol-gel Method

Figure 2 Process flow sheet for manufacturing LMO by a sol-gel process (P2) This method of manufacturing LMO involves the precipitation of a gelatinous material consisting of a lithium and manganese complex. Here, the key raw materials used for lithium and manganese sources are lithium hydroxide (LiOH) and manganese acetate (Mn(CH₃COO)₂) . In addition, ammonium hydroxide (NH₄OH) is used to assist the precipitation process. The process flowsheet for P2 is shown in Figure 2. First, Mn(CH₃COO)₂, LiOH, NH₄OH, and water are mixed in a tank at 25 °C and 1 bar to prepare the reaction mixture. The mixture is then pumped into a continuous stirred tank reactor (CSTR) operating at 25 °C and 1 bar. The mean residence time of the reacting mixture in the reactor is around 1 h. The following reaction is facilitated in the reactor with a 100% conversion.

$$LiOH + NH_4OH + 2[Mn(CH_3COO)_2.4H_2O]$$

 $\Rightarrow LiMn_2(CH_3COO)_3(OH)_2.8H_2O + NH_4(CH_3COO)_3(OH)_2.8H_2O + NH_4(CH_3COO)_3(OH)_2.8H_2O + NH_4(CH_3COO)_3(OH)_3(OH)_2.8H_2O + NH_4(CH_3COO)_3(OH$

At the completion of the aforementioned reaction, the gelatinous complex $LiMn_2(CH_3COO)_3(OH)_2$. $8H_2O$ is formed along with ammonium acetate in the reactor. The slurry consisting of the precipitate, ammonium acetate and water are heated to 90 °C and added to a vacuum dryer to remove ammonium acetate and excess water at 0.1 bar. The top product of aqueous ammonium acetate is purified and sold as a byproduct. The cost of processing and packaging is assumed to be offset by the sales of ammonium acetate and so, is excluded from the economic analysis of producing LMO. The bottom product from the vacuum drying step consisting of the precipitate is calcined in a kiln at 600 °C for 12 h. The reaction in the kiln is shown below.

$$LiMn_2(CH_3COO)_3(OH)_2.8H_2O \rightarrow LiMn_2O_4 + 6CO_2 + 13\frac{1}{2}H_2$$

A saggar-based feeding system as described in P1 is used for calcination. The calcination products are cooled at the rate of 1 °C min⁻¹ (around 10 h) to obtain the required spinel-type LMO. The particle size of the calcination product is reduced through dry milling in a ball mill to less than 44 micrometers (-325 mesh).

4. Approach and Assumptions

Spreadsheet-based process models for P1 and P2 described above were used to identify the components and parameters that significantly affect the production cost, energy demand, and environmental impact. The models include material and energy balance equations and a (capital and operating) cost calculation method. The inputs to these models are process conditions and economic parameters such as operating temperature, pressure, reaction conversions, equilibrium constants, residence times, process efficiencies, and costs for equipment and materials. The process parameters and operating conditions, if available, are obtained from the literature or estimated from the experimental data presented in various relevant patent publications. The equipment purchase costs are estimated using the expressions outlined by Turton et al.[29] and as presented in Susarla et al.[30]. The cost numbers were adjusted for the year 2018 by using the chemical engineering plant cost index (CEPCI, 603.1 for 2018). The production cost is computed using the routine proposed by Peters et al.[31] and presented by Ahmed et al.[32] and Susarla and Ahmed[33]. The relevant economic parameters for this cost model including costs for contingency, royalties, installations, construction, and other overheads as percentages of equipment cost or capital cost are assumed following the guidelines suggested by Ahmed et al.[32] and Susarla and Ahmed[33].

All procured materials are assumed to be of very high purity (battery grade). However, electrolytic manganese dioxide (EMD) is further treated in P1 to remove any traces of metal impurities present in the procured material. Also, all costs including materials and equipment are assumed to include the cost of transportation and delivery to the production site. The greenhouse gas emissions in terms of equivalent CO₂ is estimated using the Environmental Protection Agency's (EPA) greenhouse gas equivalencies calculator[34].

A baseline plant capacity of 60 metric tons (MT) per day and a plant life of 10 years for the amortization of the capital investment are assumed for the design of a production plant for spinel-type LMO material.

5. Results and discussion

The two process models (P1 and P2) developed as described above are solved to obtain production costs, bill of materials, energy required, and associated emissions. In addition, the base case scenario is perturbed to study the sensitivity of production cost to different process or model parameters and derive insights for reducing the cost.

5.1. Material and energy demand

The two processes P1 and P2 differ significantly from each other in terms of raw materials (MnO₂ or EMD and Li₂CO₃ for P1 vs. LiOH and Mn(CH₃COO)₂ for P2) and number of unit operations in the production route (6 for P1 vs. 5 for P2), as discussed earlier. P1 is primarily a solid-state synthesis approach including a pre-processing step for washing of the raw material (i.e. EMD). P2 is a sol-gel or co-precipitation method and involves a reaction stage in the synthesis process followed by drying and calcination. The main differences between P1 and P2 are washing and wet milling of EMD in P1 and reaction of raw materials, i.e. LiOH and Mn(CH₃COO)₂ in P2. After these steps, both P1 and P2 follow similar production steps for manufacturing LMO. The materials required and energy used in various steps of the two processes are listed in the Table 1.

Table 1 List of material prices and breakdown of process loads and energy demand (60 MT day⁻¹ of LMO)

			P1	P2		
Materials purchased						
MnO ₂	\$1.74 kg ⁻¹	MT day ⁻¹	61	-		
Li ₂ CO ₃	\$12.5 kg ⁻¹	MT day ⁻¹	13	-		
H_2SO_4	\$0.5 kg ⁻¹	MT day ⁻¹	1	-		
$Mn(CH_3COO)_2$	\$2 MT ⁻¹	MT day ⁻¹		171		
LiOH	\$26 kg ⁻¹	MT day ⁻¹	-	8		
NH ₄ OH	\$2 kg ⁻¹	MT day ⁻¹	-	12		
Water		MT day ⁻¹	1,493	698		
Mixing tank						
	Volume	m ³	21	41		
	Electricity	kW	42	81		
Drying						
	Heating duty	kW	192	262		
Calcination						
	Heating duty	kW	12,155	10,679		
Pumping						
	Electricity	kW	95	16		

One of the differences between P1 and P2 is in mixing of the raw materials. In P1, EMD is mixed with the lithium source in the Ball Mill 1 (see Figure 1) but in P2, all the primary raw materials (i.e. LiOH, manganese acetate, and NH₄OH) are mixed in mixer (see Fig. 2). This results in a higher volume and energy requirement for mixer in P2 (41 m³) as compared to P1 (21 m³).

Recall that 1M H₂SO₄ solution is used as the wash liquid in P1, 98% of this solution is recovered from the 1st stage of the 3-stage filter and is recycled at a representative cost[35] of \$0.15 kg⁻¹. Fresh H₂SO₄ is added to make-up the deficit and keep the dissolved impurities below the tolerance. The remaining H₂SO₄ solution is lost due to dilution with wash water primarily during the 2nd stage of the filter and so, the loss is compensated by increasing the make-up stream.

Although the drying, calcination, and milling sequence of operations is common to both processes, they differ significantly because of their operating conditions. P1 employs a spray dryer operating at 150 °C and 1 bar, whereas P2 uses a vacuum dryer operating at 90 °C and 0.1 bar. Also, the rate of evaporation in P1 (0.6 kg s⁻¹) is significantly lower than in P2 (8 kg s⁻¹.); the drying loads are 262 kW (P2) and 191 kW (P1).

Ammonium acetate recovered from the vacuum dryer in P2 is further purified to remove any trace impurities and is then sold as a byproduct. It is assumed that the revenue from the sale of this byproduct (ammonium acetate) evenly offsets the capital and processing cost required for the purification process. Thus, cost of purification or profit from sales revenue are not considered in the production cost estimation of LMO.

The calcination unit in P1 is operated at 750 °C (as compared to 600 °C in P2) with an average residence time of 20 h (as compared to 12 h for P2). A higher operating temperature and a longer residence time results in a higher energy requirement for

calcination in P1 (12,155 kW) than in P2 (10,679 kW). Note that the energy required by the furnace is estimated based on the assumption of an overall heat efficiency of 70% to incorporate the losses from the walls and the energy lost from the spent flue gas during the entire operation. It is further assumed that the furnace is operated at the rated capacity. Adjustments will need to be made if the furnace is operated at capacity lower than the rated capacity. The overall energy consumption, including electricity and process heat, for P1 is 6.2 kWh kg⁻¹ LMO as compared to 5.6 kWh kg⁻¹ LMO for P2. The washing and wet milling of EMD in P1 requires additional usage of process water. For example, wet milling alone requires addition of around 24 MT of water per day. This results in a significantly higher requirement of water by P1 (1,493 MT day⁻¹) despite being a solid-state synthesis process as compared to the wet process of P2 (698 MT day⁻¹). A higher requirement of water also translates into a higher overall pumping power required in P1 (95 kW) as compare to P2 (16 kW).

Assumption / Input Parameter	Estimated %	Of	Range %
1. Direct Costs			
A. Purchased Equipment	Model*		Model*
Installation	80%	Purchased Equipment	50-155%
B. Buildings, process and auxiliary	15%	Purchased Equipment	10-50%
C. Service facilities and yard improvements	50%	Purchased Equipment	40-80%
D. Land	8%	Purchased Equipment	4-8%*
2. Indirect Costs			
A. Engineering and supervision	10%	Direct Costs	5-20%
B. Construction expense and contractor's fee	10%	Direct Costs	5-25%
C. Contingency	5%	Fixed Cap. Investment	5-15%
3. Fixed Capital Investment = 1 + 2			
4. Working Capital	10%	Fixed Cap. Investment	10-20%
5. Total Capital Investment = 3 + 4			
I. Manufacturing Cost, \$ year ⁻¹			
A. Direct Product Costs			
Raw Materials	Model*		Model*
Operating labor	Model*		Model*
Direct supervisory and clerical labor	15%	Operating Labor	10-20%
Utilities	Model*		Model*
Maintenance and Repairs	5%	Fixed Cap. Investment	2-10%
Operating supplies	15%	Maintenance & Repairs	10-20%
Laboratory charges	10%	Operating Labor	10-20%
Patents and royalties	1%	Total Product Cost	0-6%
B. Fixed Charges			
Depreciation	Model*		Model*
Local taxes	4%	Fixed Cap. Investment	1-4%
Insurance	1%	Fixed Cap. Investment	0.6-1%
Rent	5%	Fixed Cap. Investment	5-12%
Financing	5%	Total Cap. Investment	5-10%
C. Plant Overhead Costs	5%	Total Product Cost	5-15%
II. General Expenses			
A. Administrative costs	4%	Total Product Cost	2-6%
B. Distribution and selling costs	6%	Total Product Cost	2-15%
C. R&D costs	5%	Total Product Cost	2-5%
III. Annual Cost, \$ year ⁻¹ = I + II			

Total Product Cost (\$ kg⁻¹) = Annual Cost (\$ year⁻¹)/Production Rate (kg year⁻¹) Model* - computed in the process model

5.2. Economic Analysis

The procedure for estimating total product cost is shown in Table 2 and consists of a

number of parameters and involves computing a variety of costs such as capital

investment, direct manufacturing, and general expenses.

		Process 1	Process 2
Production cost	\$ kg ⁻¹ LiMn ₂ O ₄	7.00	14.4
Sale Price (7.5 % profit)	\$ kg ⁻¹ LiMn ₂ O ₄	7.52	15.5
Purchased equipment	M\$	13	22
Materials purchased	M\$ year ⁻¹	86	187
Electricity	K\$ year ⁻¹	105	129
Water	K\$ year ⁻¹	426	199
Natural gas	M\$ year ⁻¹	1.67	1.49

Table 3 Breakdown of production costs (60 MT day-1 of LMO)

The cost of producing LMO is less for the solid-state method (P1), \$ 7 kg⁻¹ LMO, as compared to the co-precipitation method (P2), \$14.4 kg⁻¹ LMO. Assuming a profit of 7.5% on the total production cost, the sale price is estimated as \$7.5 kg⁻¹ LMO for P1 and \$15.5 kg⁻¹ LMO for P2. Table 3 lists a breakdown of the production cost for both P1 and P2 in terms of costs for equipment, materials procurement, utilities, etc. for the baseline production plant of capacity of 60 MT day⁻¹. Although the number of equipment used in P1 is more than in P2, the cost of purchased equipment for P2 is nearly twice that of P1. One of the major contributions to the total cost of equipment in both processes is the cost of their furnace system, which contributes nearly 85% of the equipment cost for P1 and 90% for P2. The furnace "system" includes the furnace, material handling equipment (e.g. saggar) and system, impurity removal system, and dust management system. The cost of furnace systems (\$10M for P1 vs. \$17.7M for P2) are a main cause for the difference in the total equipment cost between the two processes. This difference in cost is primarily due to the higher amount of material handled by P2, i.e. 7.153 kg h⁻¹, as compared to P1, 3.068 kg h⁻¹. Recall that the feed to the furnace in P2 is a lithium-manganese acetate and octahydrate complex [LiMn₂(CH₃COO)₃(OH)₂.8H₂O], whereas in P1 it is a dry homogeneous mixture of Li₂CO₃ and EMD. The capital equipment contributes \sim 3% to the total production costs for P1 and $\sim 1\%$ for P2, as seen in Figure 3. Cost of purchased materials (i.e. raw materials) is $\sim 64\%$ and $\sim 73\%$ of the total production cost (as shown in Figure 3) for P1 and P2, respectively. Clearly, the high cost of raw materials (\$86M for P1 and \$374M for P2) is the primary reason for the difference in the production costs of P1 and P2. As shown in Table 1, P1 uses EMD (\$1.74 kg⁻¹) and Li₂CO₃ (\$12.5 kg⁻¹), whereas P2 uses LiOH (\$26 kg⁻¹), manganese acetate ($$2 \text{ kg}^{-1}$), and NH₄OH ($$2 \text{ kg}^{-1}$). The price of manganese acetate is a leading reason behind the high cost of raw materials. Table 4 shows the contributions of these purchased compounds to the cost of producing the LMO.



Purchased Materials = Labor = Utilities = Depreciation = Overheads

Figure 3 Breakdown of LMO production costs

		P1	P2
MnO ₂	\$ kg ⁻¹ LiMn ₂ O ₄	1.8	
Li_2CO_3	\$ kg ⁻¹ LiMn ₂ O ₄	2.7	
$Mn(CH_3COO)_2$	\$ kg ⁻¹ LiMn ₂ O ₄		5.7
LiOH	\$ kg ⁻¹ LiMn ₂ O ₄		3.6
NH ₄ OH	\$ kg ⁻¹ LiMn ₂ O ₄		0.41
$LiMn_2O_4$	\$ kg ⁻¹	7.0	14.4

Table 4 Contribution of material costs to the production cost (60 MT day-1 of LMO)



Figure 4 Sensitivity of LMO production cost to raw material prices for P1 and P2 Considering the significant contribution of material costs to the overall production cost, the sensitivity of production cost to the prices of various raw materials is studied for both processes. Figure 4 shows the effect of change in raw material prices on the production cost of LMO for both P1 (Figure 4a) and P2 (Figure 4b). In P1, it is observed from Fig. 4a that the change in the price of either of the key materials EMD or Li₂CO₃ has a similar effect on the overall production cost of LMO. However, in P2 (Figure 4b), the price of

Mn(CH₃COO)₂ has a larger effect on the overall production cost of LMO as compared to LiOH. As seen from Table 1, the requirement of manganese acetate is nearly 171 MT day⁻¹, which is an order of magnitude higher than the other materials used in P2. This is the primary reason for the strong dependence of LMO production cost on the price of manganese acetate. On the other hand, the prices for LiOH and NH₄OH do not affect the cost of manufacturing significantly.



Figure 5 Sensitivity of LMO production cost to plant life and production capacity The effect of economies of scale and the period for capital cost amortization is assessed by studying the sensitivity of LMO production cost to the plant life (Figure 5a) and production

capacity (Figure 5b). It is apparent from Figure 5 that the change in the production cost is insignificant with respect to any change in either the production capacity or the capital amortization period. This is mainly due to the high nameplate capacity of the baseline plant, i.e. 60 MT day⁻¹. However, it is likely that economies of scale play a significant role at lower production volumes and smaller nameplate capacities. Therefore the larger production volumes considered in this study is an effective strategy for reducing the product cost.

5.3. Achieving pack-level battery cost targets

The cost targets for lithium-ion batteries are generally at the pack level. The USDOE target is to reduce the pack-level cost to less than \$100 kWh⁻¹ with an eventual aim of achieving the cost of \$80 kWh⁻¹ for an all-electric vehicle battery with around 15 min charge time and 300 mile range[1]. The production cost of LMO eventually affects this pack-level cost of a battery. The following is a discussion of the effect of the LMO cost on the pack cost.

Argonne National Laboratory developed BatPaC[2], a spreadsheet tool, to design automobile batteries using specifications such as the energy storage capacity, electrode chemistry combination, and a host of other parameters and constraints. This spreadsheetbased modeling tool (i.e. BatPaC) has been used to estimate the pack level cost of a 100 kWh and 300 kW battery, hereafter denoted as Bat100, as a function of the cost of producing LMO cathode material. Based on BatPaC analysis, around 29 MT of active material (i.e. LMO) is required for manufacturing 100,000 packs of Bat100 year⁻¹. With the LMO price of \$7.52 per kg, it contributes 22% to the cost of the battery pack (\$116 kWh⁻¹).



Figure 6 Cost of a 100 kWh and 300 kW battery in \$ kWh⁻¹ with LMO-Graphite chemistry as a function of LMO production cost and capacity of battery manufacturing facility

Figure 6 shows the cost of Bat100 consisting of LMO-Graphite chemistry as a function of the LMO production cost. A lower LMO price and higher battery production volume helps lower the pack-level cost of the battery. For the LMO price of \$7 and a battery plant with a capacity of 100,000 packs per year, the Bat100 cost is \$114 kWh⁻¹, dropping down to \$105 and \$101 kWh⁻¹ at capacities of 300,000 and 500,000 packs per year, respectively. For the three curves in Figure 6, representing the battery production volumes of 100K, 300K and 500K per year , the \$100 per kWh cost target is estimated to match at LMO prices of \$2, \$4.9 and \$6.2 kg⁻¹, respectively.

The BatPaC design of the Bat100 system using the LMO-Graphite electrode combination estimates that the LMO contributes up to 22% of the overall cost of the battery pack. Savings from other components of a battery in addition to the reduction in LMO production cost and economy of scale for battery production will be necessary to achieve the target of \$80 kWh⁻¹.

		Process 1	Process 2
Electricity	kWh day⁻¹	4,764	5,824
Max. Temperature	°C	750	600
Heat Duty	MWh day ⁻¹	370	332
Water	MT day ⁻¹	1,493	698
GHG Emissions in		72	67
Eqvt. CO ₂	MT day ⁻¹	/3	67

Table 5 Greenhouse gas emissions and Energy and water usage for manufacturing LMO

5.4. Environmental analysis

The environmental impact of the two manufacturing processes are compared in terms of their greenhouse gas (GHG) emissions, electricity consumption, water usage, and heating duty. Table 5 lists these parameters for the two processes along with the maximum temperature used in the process. The maximum temperature and calcination time for P1 is 750 °C and 20 h as compared to 600 °C and 12 h for P2. The heat duty for the two processes is comparable (370 MWh day⁻¹ for P1 vs. 332 MWh day⁻¹ for P2) because P1 requires long duration at high temperature while P2 requires the calcining of a larger quantity of material. The GHG emissions were estimated using the CO₂ equivalencies calculator[34] available on the webpage of Environmental Protection Agency (EPA). Comparable heat duties required by the two processes results in similar GHG emissions in terms of equivalent CO₂ (73 MT day⁻¹ for P1 vs. 67 MT day⁻¹). As P2 handles relatively larger materials quantities, the electricity required for pumping and other liquid handling equipment is slightly higher for P2 (5,824 kWh day⁻¹) as compared to P1 (4,764 kWh day⁻¹) ¹). One of the striking differences between the two processes is in their water requirement. P1 uses nearly twice the amount of water as compared to P2 (1,493 MT day⁻¹ vs. 698 MT day⁻¹). This is mainly because P1 requires a significantly higher amount of water for washing its key raw material (EMD). Overall, the process P1 has a relatively higher effect on the environment in terms of both GHG emissions and water usage.

6. Conclusions

The production of spinel type lithium manganese oxide (LMO) active material was studied to estimate the production cost, energy demand, and environmental impact in large volume production. Detailed process models and flowsheets were presented for two different processes. The first process involved a solid-state method, while the second process employed a co-precipitation method. The effect of reducing production cost of positive active material, LMO in this case, in achieving the US DOE mandated pack-level cost targets were evaluated.

The solid state process was found to have a significantly lower cost of production than the sol-gel process. A production cost of \$7 kg⁻¹ was estimated for the solid-state method (process 1) in a facility with production capacity of 60 MT day⁻¹. Cost of purchased materials contributed nearly 64% of the total production cost of LMO. The furnace and material handling system in furnace was the most expensive equipment and contributed nearly 85% of the purchased equipment cost. Overall energy consumption (heat and electricity) for the solid-state synthesis process was nearly 6 kWh kg⁻¹ LMO produced, where the furnace heat duty was the primary energy consuming operation. Also, the greenhouse gas emission from the solid-state method estimated from the Environmental Protection Agency's emission calculator in terms of equivalent CO₂ was ca. 1.2 kg CO₂ kg⁻¹ of LMO produced.

The U.S. Department of Energy target of \$100 kWh⁻¹ for an electric vehicle battery can be achieved for 100 kWh and 300 kW battery using LMO-Graphite chemistry by increasing the production capacity of battery manufacturing facility to more than 500,000 packs year⁻¹

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Chemical Sciences and Engineering Division

Argonne National Laboratory 9700 South Cass Avenue, Bldg. *# Argonne, IL 60439

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