

Addition of nickel cobalt aluminum (NCA) cathode material to GREET2

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1. Background

The Greenhouse gases, Regulate Emissions, and Energy use in Transportation (GREET[®]) model, vehicle cycle, contains a module to characterize the material and energy consumption associated with producing automotive lithium-ion batteries (Dunn et al. 2015).

This technical memo describes the addition of a 149 kW EV battery with a nickel cobalt aluminum cathode (NCA) material and documents the methodology used to calculate the material and energy flows used in the modeling of this cathode material in GREET. NCA is a fairly common cathode material. It has high capacity, high voltage, and well established performance which make it a promising alternative cathode material in lithium-ion batteries. According to Tanaka (2015) aluminum and cobalt contribute to the thermal stability and the electrochemical properties of this type of cathode material. This cathode material, however, is expensive to produce because of the high cost of nickel and cobalt (Doeff, 2013).

2. Material and Energy Flows in the Preparation of NCA

Figure 1 describes the production of Li-NCA cathode material based on two patents Kuang et al. (2011) and Guo and Lianqi (2014). The process is divided into two parts: 1) preparation of precursor, and 2) addition of precursor to the lithium source.

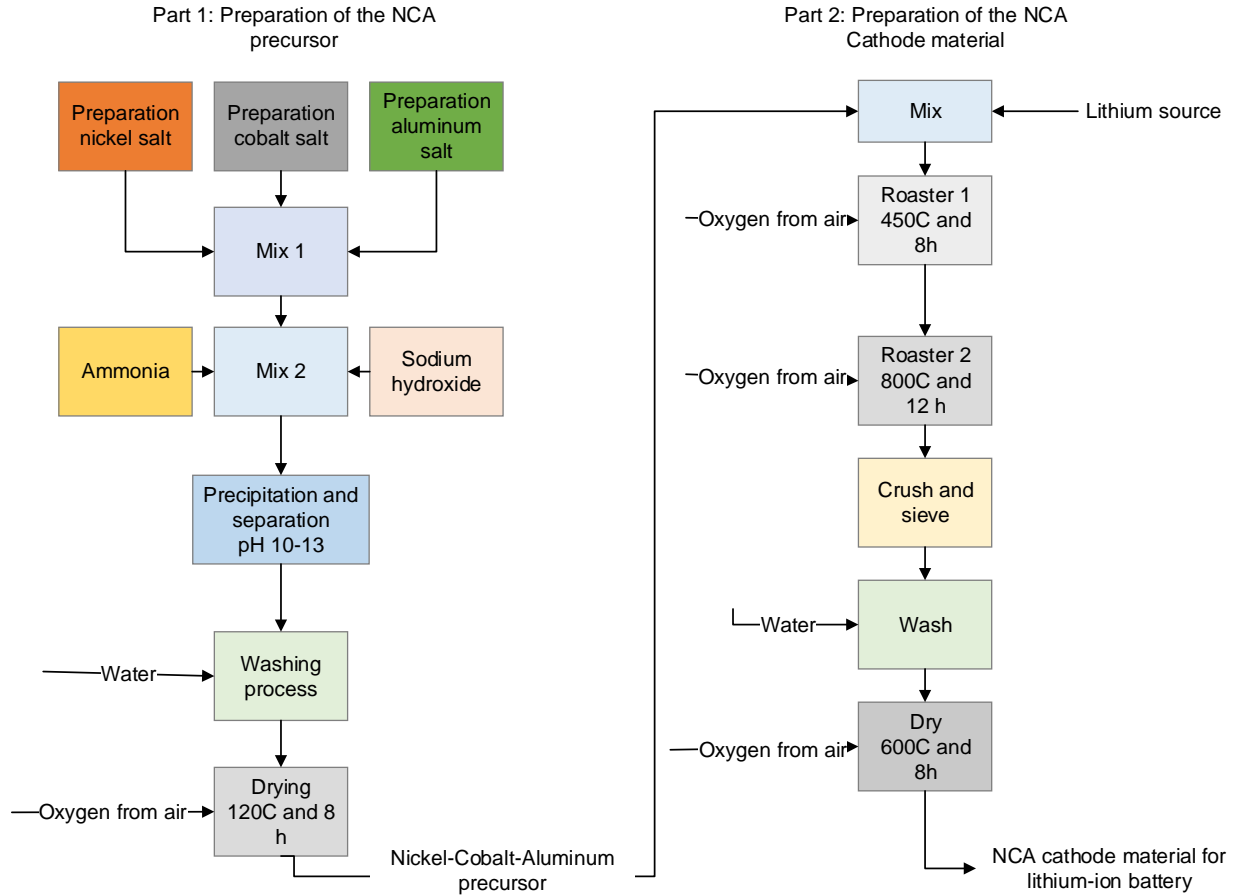


Figure 1 Production of NCA material serving as cathodic material of Lithium ion

3. Preparation of NCA precursor ($\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$)

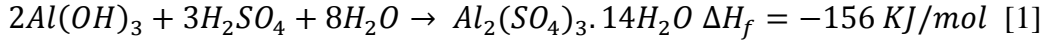
The first step of making the precursor consists of preparing a solution of 1 mol/L mixed metal ions in which the molar ratio Ni^{2+} (nickel): Co^{2+} (Cobalt): Al^{3+} (Aluminum) is 0.80:0.15:0.05 (Jian and Zhang, 2014). Different types of metal salts can be used. For instance, in the case of nickel, the inventors suggest nickel sulfate, nickel nitrate, nickel chloride, or nickel acetate, similarly, several salts were presented for the cobalt and aluminum salts (Kuang et al. 2011). We decided to use nickel sulfate (NiSO_4) and cobalt sulfate (CoSO_4) because GREET already uses these compounds in the production of NMC cathode material. The production of these two salts is also discussed in Dunn et al. (2015). However, the production of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) has not been detailed before in GREET model documentation.

Aluminum sulfate is widely used in the pulp and paper industry and in water purification. Its production is simple. The aluminium sulfate is produced according to the chemical reaction presented in Equation [1]. The raw materials used in the production of aluminum sulfate are aluminum hydroxide ($\text{Al}(\text{OH})_3$) and sulfuric acid (H_2SO_4). Table 1 presents the material input needed to produce one ton of aluminum sulfate. These values are based on stoichiometry.

Table 1 Material and energy input to produce Alumina sulfate.

Material input (ton /ton of Al₂(SO₄)₃)	
Aluminum hydroxide	0.46
Sulfuric acid	0.86

The production of aluminum sulfate involves mixing the ingredients in Table 1 with water in a reactor until the water evaporates. The reaction is exothermic. We therefore assume that no energy is consumed to carry out this reaction



Existing GREET data for sulfuric acid production can be found in (Burnham et al. 2006). On the other hand, Aluminum hydroxide (Al (OH)₃) is purified from bauxite and then precipitated by neutralization (usually with carbon dioxide) or by autprecipitation (the Bayer process). . Table 2 presents the material and energy inputs to produce one ton of aluminum hydroxide (Li et al. 2012). GREET already contains information of material and energy inputs for bauxite, limestone (Dai et al. 2015) and NaCl (Franklin Associates, 2011).

Table 2 Material and energy input to produce aluminum hydroxide (modified from Li, et al., 2012).

Material input (ton /ton of Al(OH)₃)¹	
Bauxite	1.26
Limestone	0.06
NaCl (Rock Salt)	0.04
Energy input (mmBtu/ton of Al(OH)₃)¹	
Electricity	0.25

Once the nickel-cobalt- aluminum salts are mixed, two additional solutions are added to a high-speed flow stirred reactor: 1) sodium hydroxide (NaOH) with a concentration of 1M, and 2) ammonia, which serves as a complexing agent known as (NH₃) with a concentration of 2M. The temperature in the reactor is increased from 25 °C to 60°C and the residence time is 1 hour. The pH of the reaction system is maintained between 10 and 11. A solid liquid separation is performed to obtain a solid material. This material is washed and dried in an oven at 120 °C for 8 hours. The final product is the nickel-cobalt-aluminum precursor. Table 3 presents the material and energy input needed to prepare one ton of NCA precursor. The material consumption is based on stoichiometry and the input values (i.e. molar ratio, solution concentration) provided by Guo and Lianqi (2014). Therefore, the final NCA concentration is 1 M and assuming that the reactor volume is 5000 L, the mass of precursor calculate is half a ton.

To compute the energy input of the process($q_{t,NCAOH}$), we used Equation [2] which includes the amount of energy consumed by the reactor (q_{CSTR}), stirring (q_{stir}) and drying (q_{dry}) the material.

$$q_{t,NCAOH} = q_{CSTR} + q_{stir} + q_{dry} [2]$$

Similar calculations presented in Dunn et al. (2015) were used to compute the energy consumed in the process. For example, the energy consumed by the reactor can be calculated using Equation [3], using the same assumptions: thermal conductivity for the insulation (0.04 W/mK), thickness of insulation (0.1m), surface area of the reactor (25m²). On the other hand, the energy (100 % electricity) involved in the stirring process of the reactor is assumed as 20.92 MJ/hr (Humbird et al. 2011).

$$q_{CSTR} = \frac{\lambda A (T_r - T_0) t_r}{x} \quad [3]$$

Where λ is the thermal conductivity, A is the surface area of the reactor, t_r is the reaction time, T_r is the reactor temperature, T_0 is the temperature of the wall, and x is the thickness of the insulation.

Finally, the energy to dry the material is calculated using Equation [4]:

$$q_{dry} = C_{pNCA} \Delta T \quad [4]$$

Where C_{pNCA} is the average heat capacity of NCA, which is 1.15 J/g °C (Perry and Green 1997)

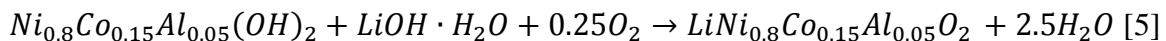
Table 3 Material and energy input to prepare 1 ton of NCA precursor

Material	Formula	ton/ton of precursor
Nickel sulfate	NiSO ₄	1.36
Cobalt sulfate	CoSO ₄	0.26
Aluminum sulfate	Al ₂ (SO ₄) ₃	0.09
Sodium hydroxide	NaOH	0.88
Ammonia	NH ₃	0.37
Energy	(mmBtu/ ton precursor)	Share (%)
Electricity	0.04	25%
Natural gas ¹	0.12	75%

¹ This energy is assumed to be provided combustion of natural gas in a boiler with an efficiency of 80%.

4. Production of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ or LiNCA

The second part of the process to produce Li-NCA cathode material consists of mixing the nickel-cobalt-aluminum precursor and the lithium source with a molar ratio of Li/ (Ni + Co + Al) = 1:1.06. According to Jian and Zhang (2014) different lithium sources can be used, including lithium hydroxide, lithium nitrate, or lithium acetate. We used lithium hydroxide (LiOH·H₂O) because this material is included in GREET. The material input for the second part of the process was calculated based on stoichiometry according to the following reaction (Equation [5]). No significant material loss was expected from this step.



The precursor and the lithium source ($\text{LiOH} \cdot \text{H}_2\text{O}$) are baked twice in two difference roasters at different temperatures in flowing oxygen to obtain $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powders. The temperature of the first roaster varies between 300 °C and 500°C for 4 to 20 hours (we assumed 450°C for 8 hours based on the patent example). The calcined material is then baked again in a second roaster for 8 to 24 hours. Temperatures for the second furnace vary between 800 and 950°C (we assumed 850°C for 12 hours based on the patent example). Finally, the calcined material is crushed, sieved, and washed with water, then dried again at 600°C for 8 hours. The final product is a nickel-cobalt-aluminum lithium material filtered through a 500-mesh sieve. The characteristics of the final product are: average particle size of 6.8 μm , a tap density of 2.74g/cm³, the highest available packing density 3.65g/cm³, decomposition temperature of 260°C (Jian and Zhang, 2014). Table 4 presents the material and energy input needed to prepare a ton of LiNCA cathode material. Once again, the material consumption is obtained based on stoichiometry and the input values provided by Jian and Zhang (2014). The reactor volume assumed was 8300L (Majeau-Bettez et al, 2011) to obtain a final amount of LiNCA of 25 tons. The energy calculation for this step of the process involves the amount of energy needed to heat: 1) the material (q_{material}), and 2) the two ovens or roasters (q_{oven}) during the baking process. It also includes the amount of energy needed to dry the material after been washed. This calculation is summarized in Equation [6]. Similar assumptions presented in Dunn et al. (2015) were used to compute the heat demand, for instance, Equation 7 and Equation 8 of the report by Dunn et al. (2015) are used to compute q_{material} and q_{oven} , respectively. Equation [4] is used to compute q_{dry} . Energy requirements for crushing and pelleting were ignored.

$$q_{\text{total,NCA}} = q_{\text{material}} + q_{\text{oven}} + q_{\text{dry}} \quad [6]$$

Table 4 Material and energy input to prepare 1 ton of LiNCA cathode material

Material input (ton/ton of LiNCA)	
NCA – precursor	0.95
LiOH – Lithium hydroxide	0.25
O ₂	0.04
Energy input (mmBtu/ton LiNCA)	
Electricity	1.51

Finally, from GREET calculations the total fossil fuel consumed in the process was 137 MMBtu per ton of LiNCA produced and the GHG emissions are 10,644 Kg of CO₂e per ton of LiNCA produced.

5. Incorporation of a NCA electric vehicle battery in GREET

To generate the material inventory for an NCA EV battery with a power of 149 kW and an energy of 28 kWh (Dunn et al. 2014), we applied the Battery Production and Cost (BatPaC) model as we have in the past. The material inventory is in Table 5. The total weight of the battery is 172 kg.

Table 5. Inventory of components of NCA EV battery (BatPaC model)

Component	Mass % ^a
NCA	28%
Graphite	19%
Binder	2.5%
Copper	11%
Aluminum	20%
LiPF ₆ (electrolyte)	1.9%
Ethylene carbonate (electrolyte)	5.4%
Dimethyl carbonate (electrolyte)	5.4%
Polypropylene	1.6%
Polyethylene	1.2%
Polyethylene terephthalate	1.4%
Steel	0.4%
Thermal insulation	0.4%
Glycol	1.0%
Electric parts	1.6%

a. Total may not sum to 100% because of rounding

6. References

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