U.S. Department of Energy
Advanced Research Projects Agency – Energy (ARPA-E)

Request for Information (RFI)
DE-FOA-0003386
on
Industrial Chemistry and Process Innovations to Enable Continuous, Waste-Free, Domestic Manufacturing of Critical Battery Cathode Active Materials

Introduction:

The purpose of this Request for Information (RFI) is to solicit input for a potential ARPA-E program focused on leveraging material, process, equipment, and cross-supply chain manufacturing innovations to catalyze domestic production of cathode active materials (CAMs) and their precursors (pCAMs). Recent legislation in the United States incentivizes domestic production of electric vehicles (EVs) and onshoring of the EV battery supply chain.[1,2] A key step in the EV battery supply chain is the production of pCAM and CAM. Presently, production of both pCAM and CAM is heavily concentrated outside the U.S., and two foreign companies control a majority of the global pCAM market.[3] Domestic pCAM and CAM production would bolster U.S. energy security and enable the creation of secure and resilient critical mineral supply chains. However, present pCAM production methods generate large volumes of hazardous waste (e.g., sulfates) and suffer from limited throughput (less than 25 kilotons per annum per facility on average).[4] Subsequent conversion of pCAM into CAM relies on energy-intensive, high-temperature processing methods that suffer from limited throughput. Energy intensity and limited throughput for conventional methods are among major hurdles to domestic CAM production. As a result, new innovations in pCAM and CAM manufacturing are needed to develop scalable and sustainable domestic EV battery supply chains.

Despite recent growth of the EV market, relatively few new companies have entered the pCAM market. This is likely because pCAM synthesis is a low-margin business, involves variable operating costs due to fluctuations in raw material prices, and is challenging to permit due to regulatory factors. Efforts to create a domestic pCAM and CAM supply chain should focus on inspiring new commercial manufacturing paradigms for pCAM and CAM, rather than reverse engineering existing practices. For domestic commercial implementation, new innovations in pCAM and CAM synthesis must afford materials whose quality and economics are commensurate, but preferably superior to, presently available options. Future chemical process roadmaps for domestic pCAM and CAM production must consider factors such as throughput, energy efficiency, hazardous waste generation, and domestic raw material supply, among others. Finally, the primary CAMs of interest to this RFI are lithium-based

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[1] "Infrastructure Investment and Jobs Act", H.R. 3684, 117th Congress, November 15, 2021. https://www.congress.gov/bill/117th-congress/house-bill/3684/text.
[2] "Inflation Reduction Act of 2022", H.R. 5376, 117th Congress, August 16, 2022. https://www.congress.gov/bill/117th-congress/house-bill/5376/text/eas.
[3] "CNGR Advanced Material and Huayou Cobalt Have Secured Orders for Ternary Precursors from Tesla", EnergyTrend, August 8, 2022, https://m.energytrend.com/news/20220808-29569.html.
[4] Rechenberger, Daniela, and Sophie Lyu. "BASF and Shanshan to Form a Joint Venture Serving the Largest Battery Materials Market, China." BASF, May 20, 2021. https://www.basf.com/hk/en/media/news-releases/global/2021/05/p-21-215.html.

chemistries that have been validated for commercial deployment in EVs and consumer electronics [e.g., lithium nickel manganese cobalt oxide (NMC), lithium nickel cobalt aluminum oxide (NCA), lithium iron phosphate (LFP)].

Areas of Interest for Responses to this RFI:

Concepts specifically of interest to this RFI, either alone or in combination, include but are not limited to the following:

- Continuous flow reactors and processes for pCAM production
- One-pot, continuous flow reactors and processes for combining pCAM and CAM production into a single step
- Production pathways that incorporate process intensity by combining two or more individual steps and/or eliminate the requirement for one or more steps without compromising pCAM/CAM quality
- pCAM produced from abundant and low-cost precursors sourced domestically
- pCAM processing that uses conventional or modified precursor strategies but can tolerate lower-grade feedstocks without compromising pCAM/CAM properties
- Significant reduction and/or complete elimination of hazardous waste types and volumes during pCAM production
- Processes that improve the energy efficiency of pCAM/CAM production
- Processes and practices that can achieve significantly increased pCAM/CAM throughput
- pCAM/CAM production concepts that can be integrated and practiced at large commercial scales
- Extreme, process-intensive, and continuous production methods that remove, eliminate, or combine steps in the supply chain (e.g., direct ore conversion routes)
- Circular techniques that utilize and/or valorize all waste and emission streams

Areas Not of Interest for Responses to this RFI:

Information specifically not requested at this time includes:

- "Next-generation" and/or exploratory battery cathode materials and chemistries that have not been extensively validated in commercial applications
- Obvious process solutions that represent incremental improvements in conventional pCAM and/or CAM production
- Incremental improvements in batch production methods for pCAM and/or CAM materials
- Concepts that lead to higher overall production costs compared to conventional processes
- Process solutions that generate hazardous waste at volumes and/or toxicity greater than conventional practices for producing pCAM/CAM
- Concepts that require expensive and/or supply chain-constrained raw materials
- pCAM/CAM production that requires highly customized equipment that cannot be manufactured and/or procured at required sizes/volumes

RFI Guidelines:

CAREFULLY REVIEW ALL RFI GUIDELINES BELOW. Note that the information you provide will be used by ARPA-E solely for program planning, without attribution. **THIS IS A REQUEST FOR INFORMATION ONLY. THIS NOTICE DOES NOT CONSTITUTE A FUNDING OPPORTUNITY ANNOUNCEMENT (FOA). NO FOA EXISTS AT THIS TIME.**

The purpose of this RFI is solely to solicit input for ARPA-E consideration to inform the possible formulation of future research programs. ARPA-E will not provide funding or compensation for any information submitted in response to this RFI, and ARPA-E may use information submitted to this RFI without any attribution to the source. This RFI provides the broad research community with an opportunity to contribute views and opinions.

No material submitted for review will be returned and there will be no formal or informal debriefing concerning the review of any submitted material. ARPA-E may contact respondents to request clarification or seek additional information relevant to this RFI. All responses provided will be considered, but ARPA-E will not respond to individual submissions or publish publicly a compendium of responses. **Respondents shall not include any information in the response to this RFI that could be considered proprietary or confidential**.

Responses to this RFI should be submitted in PDF format to the email address **ARPA-E-RFI@hq.doe.gov** by **5:00 PM Eastern Time on Wednesday, July 10.** Emails should conform to the following guidelines:

- Insert "<your organization name> - Response to Domestic Manufacturing of pCAM-CAM Materials" in the email subject line.
- In the body of your email, include your name, title, organization, type of organization (e.g., university, non-governmental organization, small business, large business, federally funded research and development center [FFRDC], government-owned/government-operated [GOGO]), email address, telephone number, and area of expertise.
- Responses to this RFI are not page-limited (use 12-point font size).
- Responders are strongly encouraged to include preliminary results, data, and figures that describe their potential materials, designs, or processes.

Technical Background:

Most commercial lithium-ion batteries employ graphite anodes and layered transition metal oxide cathodes. CAMs can account for approximately 50% of total battery cost, while CAM chemistry determines overall battery performance and safety.[5] To date, commercial cell-level energy densities exceeding 280 watt-hour per kilogram (Wh/kg) are achievable in batteries where NMC is used as the CAM in combination with a graphite anode.[6] Recent optimization efforts have focused on innovations in

[5] Govind Bhutada, "Breaking Down the Cost of an EV Battery Cell", Elements, February 22, 2022, https://elements.visualcapitalist.com/breaking-down-the-cost-of-an-ev-battery-cell/.
[6] "The Beginning of Commercial Vehicle Innovation", LG Energy Solution, https://www.lgensol.com/assets/file/202312_LGES_Commercial_EV_Catalog_en.pdf.

chemistry to decrease cobalt content and increase nickel content thus simultaneously increasing energy density and reducing cost. Moreover, significant government and private sector research funding has been allocated to develop alternative lithium-based battery chemistries. Thus far, LFP is the most commercially successful nickel-free and cobalt-free cathode to be developed with notable attributes in cost, safety, and cycle life. Recent gains in market share suggest that LFP batteries may become the dominant chemistry for compact, economy EVs, while NMC is likely to continue to be the preferred cathode chemistry for vehicles where torque response and range are priorities.[7]

The first step in the CAM supply chain is the mining and refining of raw materials. In the case of NMC, this includes processing nickel, manganese, and cobalt ores, which are largely mined and processed outside the U.S. Nickel, manganese, and cobalt concentrates are then converted into sulfates through a series of steps, including flotation, smelting, refining, acid leaching, separation, and purification. pCAM is synthesized via a co-precipitation process, which is followed by calcination (lithiation and oxidation) to afford the final CAM.[8] To synthesize pCAM, metal sulfates are reacted via co-precipitation to form a mixed-metal hydroxide complex ($Ni_xCo_yMn_{1-y-x}(OH)_2$), as shown Figure 1. This co-precipitation generates significant quantities of hazardous liquid waste. The key figure of merit for pCAM producers is product homogeneity since this drives the quality and performance of the final CAM (and battery) product. Precursor synthesis is a standardized process; small changes in reaction conditions (e.g., pH, temperature) and practices (e.g., batch size, process time) have significant impacts on product homogeneity. While both batch and continuous processes are possible, a batch process is preferred because it yields better product homogeneity, despite limited throughput.

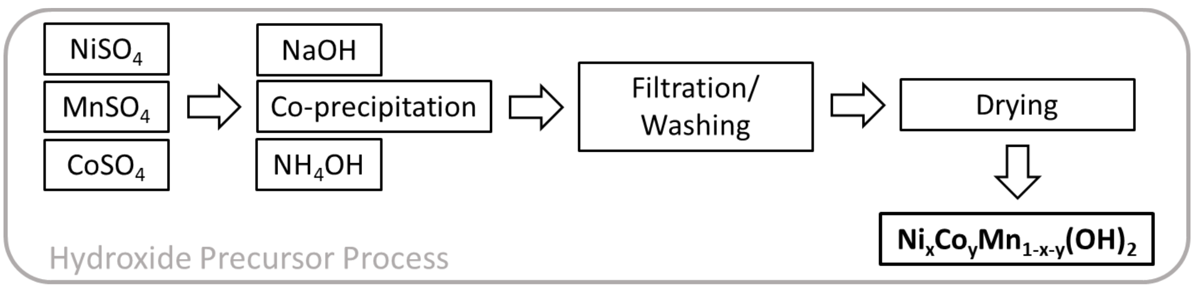

Figure 1. Synthetic pathway to the hydroxide precursor of NMC (pCAM).

Next, lithium ions are inserted into the metal hydroxide lattice during a high-temperature solid-state synthesis step for converting pCAM to CAM (Figure 2). First, pCAM is mixed with solid lithium hydroxide (LiOH) and/or lithium carbonate (Li_2CO_3) in a dry mix process. At this stage, a modest excess of lithium (typically less than 10%) is added to the mix to compensate for evaporative losses during the subsequent high temperature treatment. Partially because lithium insertion is a kinetically limited and thermodynamically uphill reaction, this step is energy intensive [5-10 kilowatt-hour (kWh)/kg CAM].[9]

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[7] "Global EV Outlook 2023", International Energy Agency, https://www.iea.org/reports/global-ev-outlook-2023.

[8] Jennifer B. Dunn, Christine James, Linda Gaines, Kevin Gallagher, Qiang Dai and Jarod C. Kelly, "Material and Energy Flows in the Production of Cathode and Anode Materials for Lithium Ion Batteries", Argonne National Laboratory, https://publications.anl.gov/anlpubs/2015/10/121442.pdf.

[9] Qiang Dai, Jarod C. Kelly, Jennifer Dunn and Pahola Thathiana Benavides, "Update of Bill-of-materials and Cathode Materials Production for Lithium-ion Batteries in the GREET Model", Argonne National Laboratory, https://greet.anl.gov/publication-update_bom_cm.

Calcination at temperatures greater than 800 degrees Celsius is carried out using precisely controlled reaction parameters including process temperature and temperature profiles, atmospheric composition and homogeneity, and residence time. Next, grinding is used to reduce particle size after calcination to afford a CAM powder. Finally, specialty coatings may be deposited on the surface of NMC particles to improve stability during battery cycling.

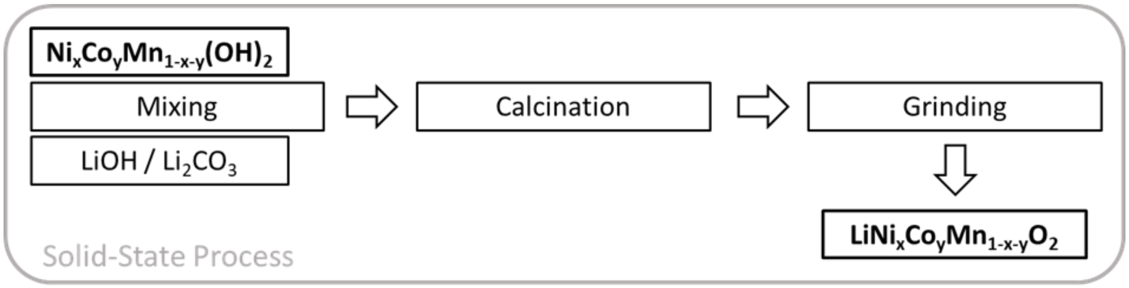

Figure 2. Solid-state synthesis and post processing for Li-NMC (CAM).

While the above discussion is focused on NMC, it should be noted that CAM synthesis for some alternative chemistries follow an analogous approach. As a result, pCAM/CAM processing innovations for NMC may benefit LFP, NCA, and other commercial and next generation CAM chemistries.

<u>RFI Questions:</u>

The questions posed in this section are organized into several different groups. Respondents may provide responses and information about any of the following questions. **ARPA-E does not expect any one respondent to answer all, or even many, of the prompts in this RFI.** In your response, please indicate the question number in your response (e.g., Response to RFI Question 1). Appropriate citations are highly encouraged. Respondents are also welcome to address other relevant avenues or technologies that are not outlined below, except for those that fall under the "Areas Not of Interest for Responses to this RFI" described above.

<u>Topic A: pCAM Feedstock Considerations</u>

1) Presently, pCAM and CAM production companies work together closely, yet mining companies are largely excluded due to the industry's aversion to differentiated goods and lack of expertise.
    - What technologies and innovations can be used to incentivize upstream raw material providers to enter the pCAM manufacturing market?
    - What other options and/or methods exist for sourcing pCAM feedstocks beyond mining?
    - How readily available are domestic pCAM feedstocks and how much can realistically be recovered from domestic sources?
2) What are the challenges and potential solutions to recycle feedstock materials for pCAM?
    - How and to what extent can the required grade of pCAM feedstocks be recovered through conventional recycling techniques?
    - What are the licensing, processing, qualification, and economic challenges?
3) What practical alternatives to sulfates as the primary class of pCAM feedstock exist? What is the validated quality of pCAM prepared from these alternatives compared to the present state of the art?

Topic B: pCAM Manufacturing

4) A key constraint to scaling pCAM synthesis via existing technologies is the limited throughput for mixed-metal hydroxide preparation.
    - What batch or continuous process alternatives to co-precipitation can increase pCAM production throughput?
    - What alternative methodologies have been validated beyond the laboratory scale?
    - What barriers, if any, to scalability exist for these alternative approaches?
    - Are there any licensable methods or processes covered in the patent literature?
5) What new synthetic pathways can be designed that are more amenable to continuous pCAM processing without compromising quality?
    - Provide examples of pCAM prepared from continuous processing. Compare the performance of the corresponding CAM to materials fabricated from pCAM produced via batch processing.
    - What barriers, if any, exist for scaling continuous processing of pCAM?
    - What commercial specifications should be used to define pCAM quality?
6) The current pCAM synthesis approach generates significant quantities of liquid sulfate waste, which limits permitting viability in the U.S.
    - Can closed-loop processes be designed to mitigate waste?
    - To what extent can sulfate-free feedstocks be used?
    - What circular routes are available?

Topic C: CAM Manufacturing

7) Throughput is a challenge for CAM manufacturing.
    - What innovative lithiation/calcination strategies can be scaled to improve the throughput of CAM manufacturing?
    - What are the alternatives to conventional roller hearth kilns that can be implemented at scale to reduce calcination intervals and achieve higher throughput for CAM production?
    - What is the typical emissions inventory associated with these strategies?
8) CAM production is energy intensive due in part because lithiation of the mixed-metal hydroxide is thermodynamically unfavorable and kinetically limited.
    - Can the rate of this solid-state reaction be increased without additional energy inputs or with minimal energy increase?
    - Alternatively, how might the activation barrier for this reaction be reduced? What other lithium sources can be utilized?
    - Through which strategies can energy efficiency be improved (e.g., combining steps)?
9) For responses to questions that describe one or more process innovations that align with the interests of this RFI, what material-level specifications can be (or have been) achieved in practice (e.g., range of compositions and compositional purity, physical properties, phase types, electrochemical performance, other factors)? Use available commercial specifications for CAMs as context, whenever possible.
10) What other foreseeable pathways exist to provide industry-specified CAMs that do not employ conventional methods and precursors yet reside within the scope of this RFI? What hurdles stand in the way of commercializing these options?