PROCESS R&D FOR MANUFACTURING OF AQUEOUS REDOX FLOW BATTERY MATERIALS

Kris Pupek and Trevor Dzwiniel
Materials Engineering Research Facility
Applied Materials Division
Argonne National Laboratory

October 12, 2022
ARGONNE’S MATERIALS ENGINEERING RESEARCH FACILITY (MERF)
A TECHNOLOGY CENTER FOR MATERIALS MANUFACTURING R&D

- Established in 2009, remodeled and expanded in 2019
- About 28,000 sq. ft. of labs, offices and collaborative space
- Over 40 scientists, engineers and supporting staff
HOW MERF CAN HELP YOUR MATERIAL NEEDS
PREPARE, EVALUATE AND PROVIDE COMPLEX MATERIALS

 To accelerate the development of new materials, processes and manufacturing science-driving innovation from invention to commercialization.

 We do this by applying science and engineering to address challenges, bridging fundamental research through commercial manufacturing to meet the advanced materials needs of the future.

 We apply advanced synthesis and processing protocols to develop new routes for scalable manufacturing procedures for newly invented experimental materials.

 Make kilogram quantities of the material available for industrial evaluation, prototyping, device level validation and to support further research.

 We apply emerging manufacturing technologies and use science-based, data-driven techniques for manufacturing intensification.
MERF SUPPORTING PNNL FOR PROCESS R&D AND SCALE UP

Timeline
- Project start date: Oct. 2019
- Project end date: Ongoing

Budget
- Project funding:
  - $60,000 in FY19
  - $100,000 in FY21
  - $100,000 in FY22

Barriers to address
- New non-metal electrolytes are needed for advanced redox flow batteries to address supply chain shortage.
- High cost of manufacturing advanced materials needs to be addressed.
DHSP – PNNL GEN I AQUEOUS REDOX FLOW BATTERY MATERIALS

- We previously scaled up PNNL developed material (DHPS) and 2kg was produced in 20L reactors.
- Argonne MERF utilizes capability and expertise in process R&D and scale up to produce kilogram materials for prototyping and device level demonstration and validation.
- The key step, a sulfonation reaction was a high hazard process that was carried out at 145°C in concentrated sulfuric acid in 20 L reactor.
- Development addressed hazardous sulfonation conditions, and gave reproducibly pure material.
- Argonne’s MERF staff with industrial experience carried out the operation in a safe way producing high purity material in a timely fashion.

\[
\begin{align*}
\text{NH}_2 \quad \text{NH}_2 & \quad \text{H}_2\text{SO}_4 \quad \text{HO}_3\text{S} \quad \text{NH}_2 \\
\text{OH} & \quad \text{H} \quad \text{OH} \\
\end{align*}
\]
1,3-DHP is a new material PNNL selected for in FY22 process R&D and scale up.

Methods of producing 1,3-DHP have appeared several times in the chemical literature. As shown here, Yosioka and coworkers produced 1,3-dimethoxyphenazine in low yield by condensing aniline and 4-nitroresorcinol dimethylether with potassium hydroxide in refluxing toluene. This intermediate, 1,3-dimethoxyphenazine, was then demethylated using hydrobromic acid in acetic acid to yield the target 1,3-DHP. The yield of 1,3-DHP produced in the demethylation step was not reported and are presumable very low.

As shown in the bottom scheme, Clemo and Daglish report the synthesis of 1,3-DHP via the hydrolysis of 1,3-diaminophenazine. The hydrolysis step proceeds in 20% yield leading to an overall 9% yield from a starting material of picaryl-o-phenylenediamine.

Neither of the processes were suitable for larger scale synthesis.
1,3-DHP – AN AQUEOUS REDOX FLOW BATTERY MATERIAL

- Argonne’s MERF helped PNNL project to meet milestones (FY22) by scaling up another new material.
  - Two-step process was evaluated and process R&D was run to determine optimal and safe procedure.
  - To achieve desired scale of 1.5 kg in a single batch, 50L CSTR reaction vessel was used.
  - Development optimized the first low-yielding step.
  - 3 kg of intermediate 1,3-DHPO was made and isolated.
  - Overall, 2 kg of high purity material was produced and delivered to PNNL for prototyping and device level validation.

- In both steps, development was needed to address issues not observed in small scale processes.
NEW ORGANIC REDOX FLOW BATTERY MATERIALS IN CONSIDERATION

- Two new materials are under development in PNNL.
- Both involve high-hazard processes to scale up.
- Argonne’s MERF already evaluated the processes and assessed scalability.
- Argonne’s MERF capability and personnel skills in the area of organic chemicals process R&D and scale up are unique to national labs complex.
- The facility and its personnel enables smooth transition from discovery to material and devices validation.
- We work closely with discovery scientists to turn their concept work into actual products to benefit society.
CONCLUSION, NEXT STEP AND ACKNOWLEDGEMENT

- Our mission is to help discovery scientist turn their discovery into commercial product.
- Argonne’s Materials Engineering Research Facility (MERF) researchers and engineers have industrial experience, a expertise and capability to run process R&D and scale up newly developed advanced materials.
- MERF provides sufficient amount of materials for device-level evaluation as well as detailed process description for accurate manufacturing cost estimation.
- We are open to collaborations and ideas.

- The two new materials evaluated by PNNL will be scaled up to kg+ and provided for performance validation.
- We will work with PNNL on scaling up any future materials currently under development.

- Continuous support from Dr. Imre Gyuk, Director of Energy Storage Research in the DOE Office of Electricity is gratefully acknowledged.