Argonne NATIONAL LABORATORY

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

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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.

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MERF SUPPORTING PNNL FOR PROCESS R&D AND SCALE UP

Timeline

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

Budget

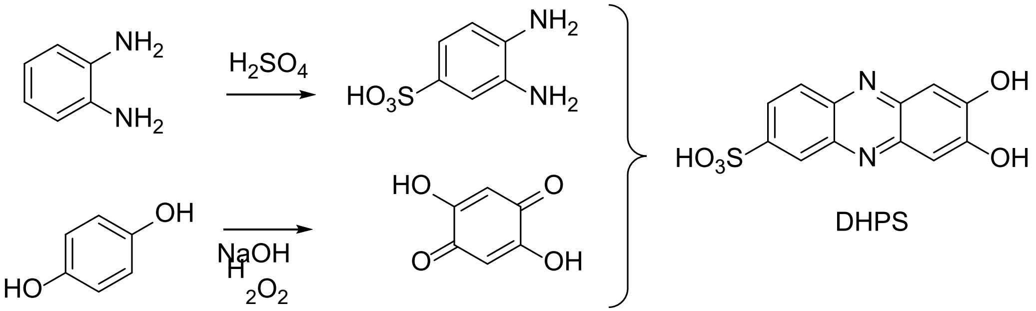
- Project funding:
  - $60,000 in FY19
  - $100,000 in FY21
  - $100,000 in FY22

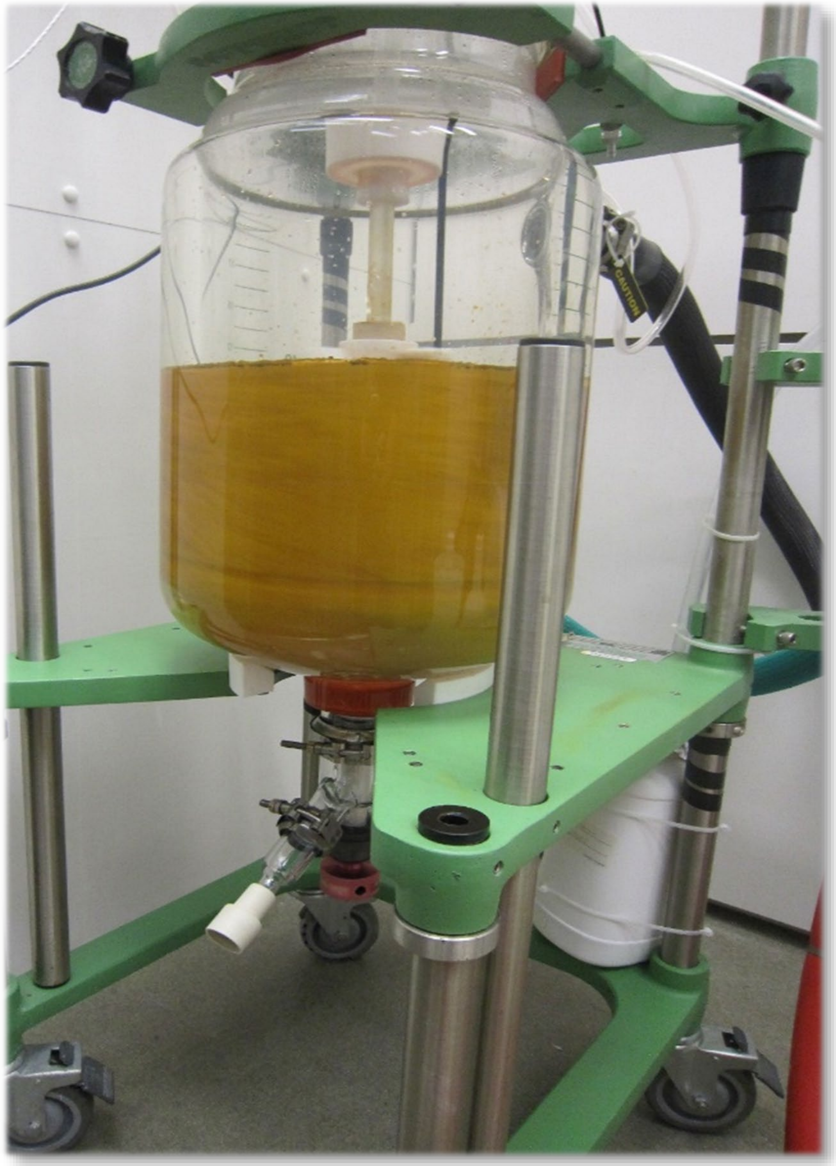
Barriers to address

- 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.

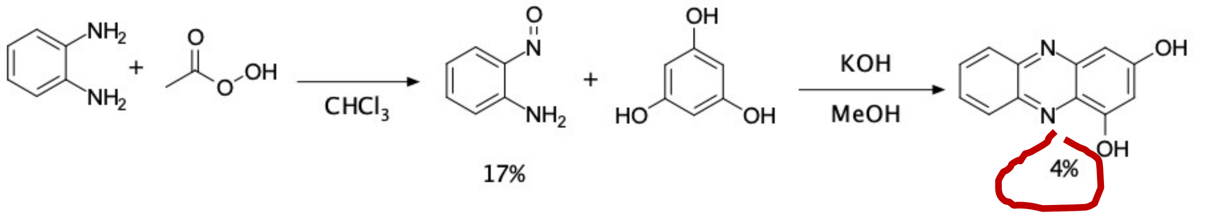
DHSP – PNNL GEN I AQUEOUS REDOX FLOW BATTERY MATERIALS

- 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 145ºC 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.

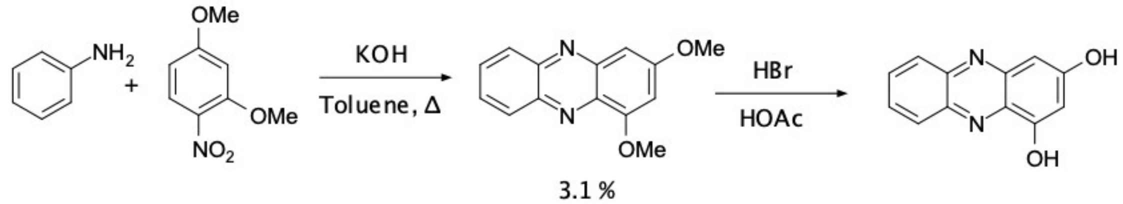




1,3-DHP – AN AQUEOUS REDOX FLOW BATTERY MATERIAL



A.



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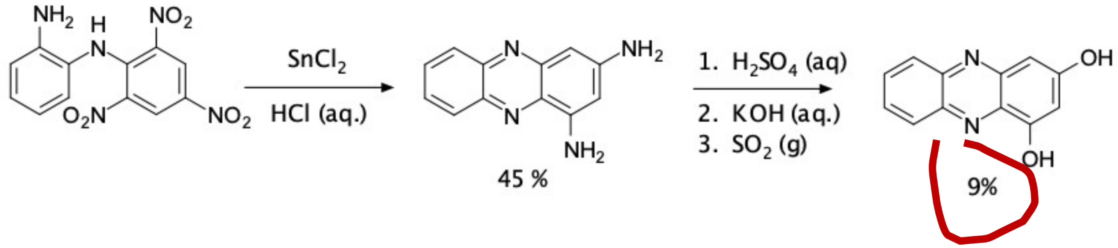


Neither of the processes were suitable for larger scale synthesis

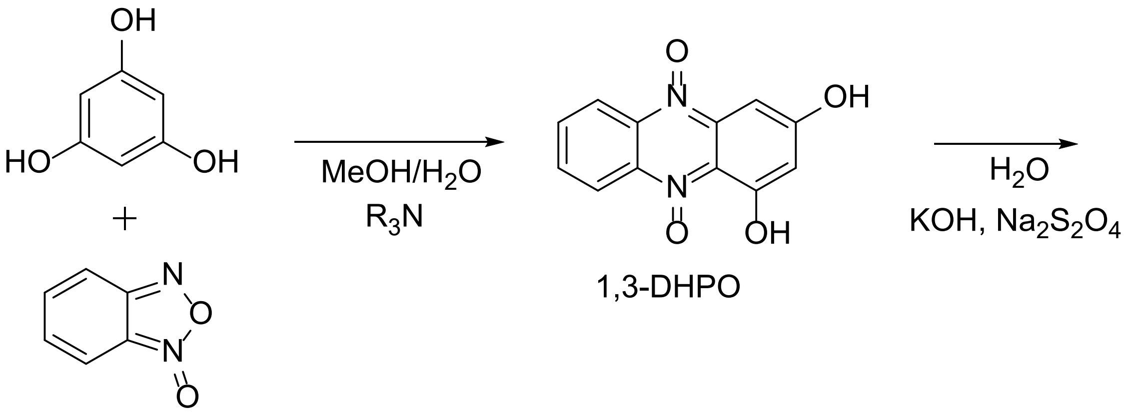
1,3-DHP is a new material PNNL selected for in FY22 process R&D and scale up.

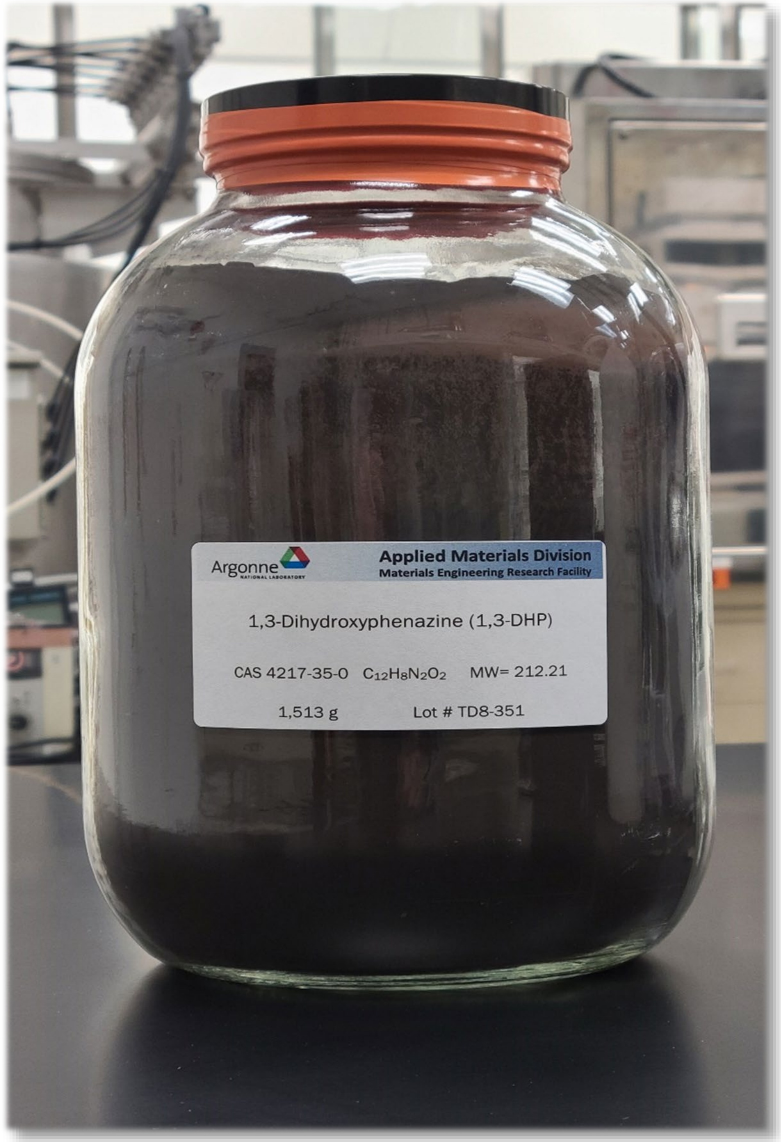
Methods of producing 1,3-DHP have appeared several times in the chemical literature. As shown here, Yosioka and coworkers produced 1,3-dimethoxyphenazine in low yield by condensing aniline and 4-nitroresorcinol dimethylether with potassium hydroxide in refluxing toluene. This intermediate, 1,3-dimethoxyphenazine, 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.

1,3-DHP – AN AQUEOUS REDOX FLOW BATTERY MATERIAL

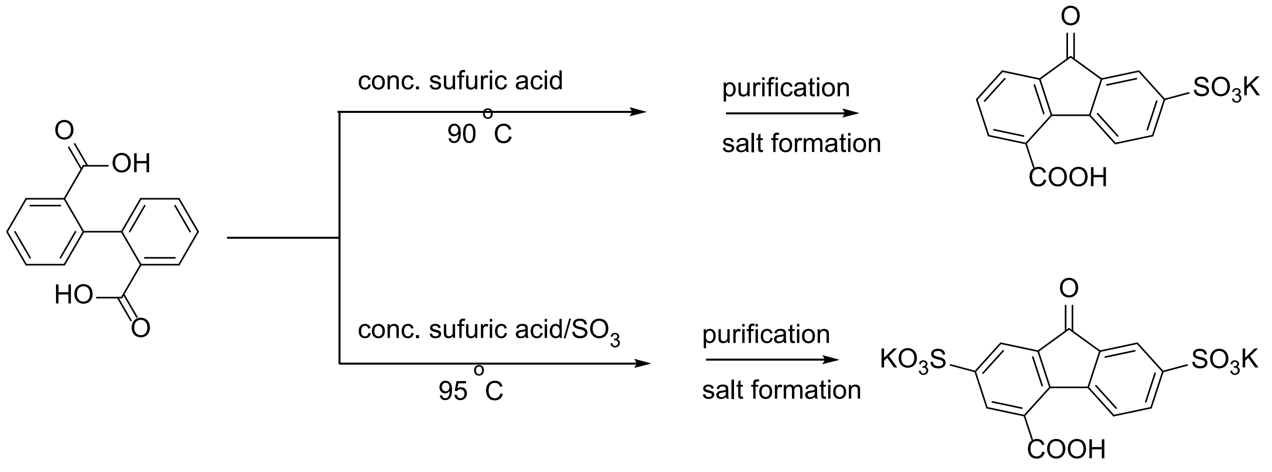
- Argonne's MERF helped PNNL project to meet milestones (FY22) by scaling up another new material.
  - Two-step process was evaluated and process R&D was run to determine optimal and safe procedure.
  - **To achieve desired scale of 1.5 kg in a single batch, 50L CSTR reaction vessel was used.**
  - Development 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 expertize 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.**