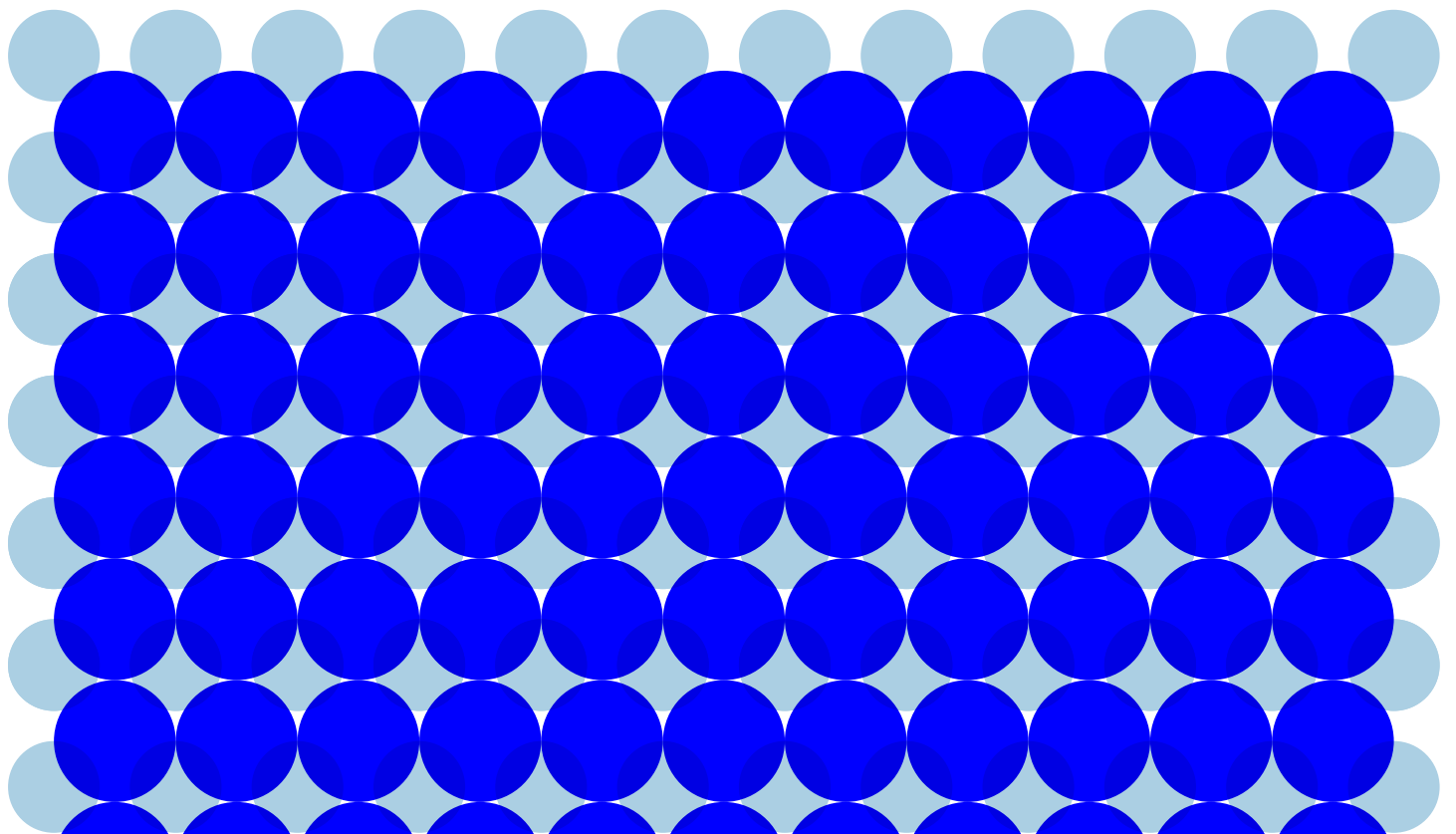


Innovations in battery energy storage: the role of ferrocyanides in advancing technology

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The global battery industry is experiencing a remarkable transformation. This is driven by plummeting prices, technological advancements and more affordable minerals, particularly lithium. Due to the expanding market, the industry continues to seek and test new chemistries to increase the efficiency, safety, and eco-friendliness of energy storage systems. How can Arxada contribute to the advances in the energy storage industry?



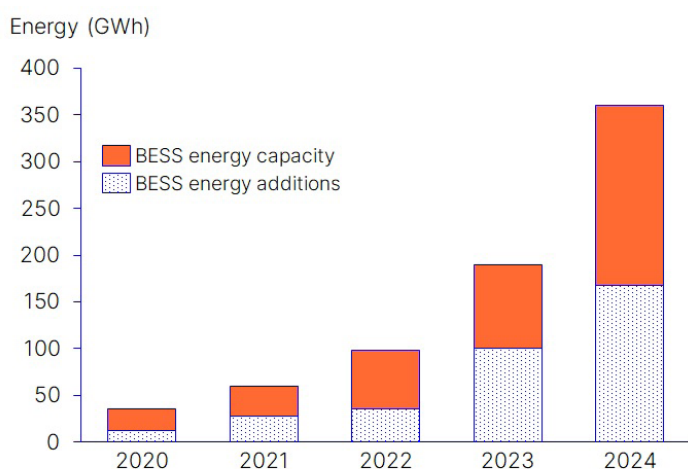
Innovations in battery energy storage: the role of ferrocyanides in advancing technology

The battery energy storage systems (BESS) market is rapidly evolving due to the need for integrating renewable energy sources and improving grid stability. Global energy storage capacity additions are expected to reach between 500 and 700 gigawatt-hour by 2030, driven by supportive policies and favorable market conditions in regions like North America, Europe, and China^{1,2}. The decline in battery costs has further enhanced the competitiveness and feasibility of energy storage solutions. Looking ahead, the market is set to expand, fueled by industrial policies and technological advancements aimed at making energy storage more efficient and cost-effective, supporting the transition to a sustainable energy future.

While lithium-ion batteries (LIBs) remain the dominant technology³, new alternatives such as sodium-ion (SIBs) and redox-flow (RFBs) batteries are emerging, while most alternative battery technologies such as solid state batteries are still at a relatively low level of technology readiness⁴. Some of these technologies rely on materials such as ferrocyanides like Sodium Ferrocyanide, or Prussian blue (PB) and Prussian blue analogues (PBAs), which offer scalability at low cost due to the abundance of key raw materials. The emerging technologies offer new solutions, particularly in stationary energy storage, and might potentially complement LIBs for specific applications.

Arxada is well-positioned to support industry growth with its large-scale, backward-integrated cyanide operations in Switzerland, proven ability to scale battery-grade materials like Prussian blue, and flexible CDMO (Contract Development and Manufacturing Organization) approach to meet customer demand and ensure high product quality.

Figure 1. Development of the BESS storage capacity and additions between 2020-2024¹.



Ferrocyanides are inorganic compounds that contain the ferrocyanide ion - $[\text{Fe}(\text{CN})_6]^{4-}$, a coordination complex of one centered atom of iron (Fe^{2+}) and six anions of cyanide (CN^-) groups, forming an octahedral structure. Ferrocyanides have found various applications over the centuries, such as pigments in many industries, anti-caking agent in food industry, water treatment, analytical chemistry or catalysis⁵. Recently, ferrocyanides have gained significant attention in the energy industry, especially in the context of energy storage technologies due to their unique electrochemical properties, affordability and availability of raw materials. Ferrocyanides such as Prussian blue (PB) and Prussian blue analogues (PBAs) have been explored for a variety of applications such as electrode materials or in electrolyte formulations.

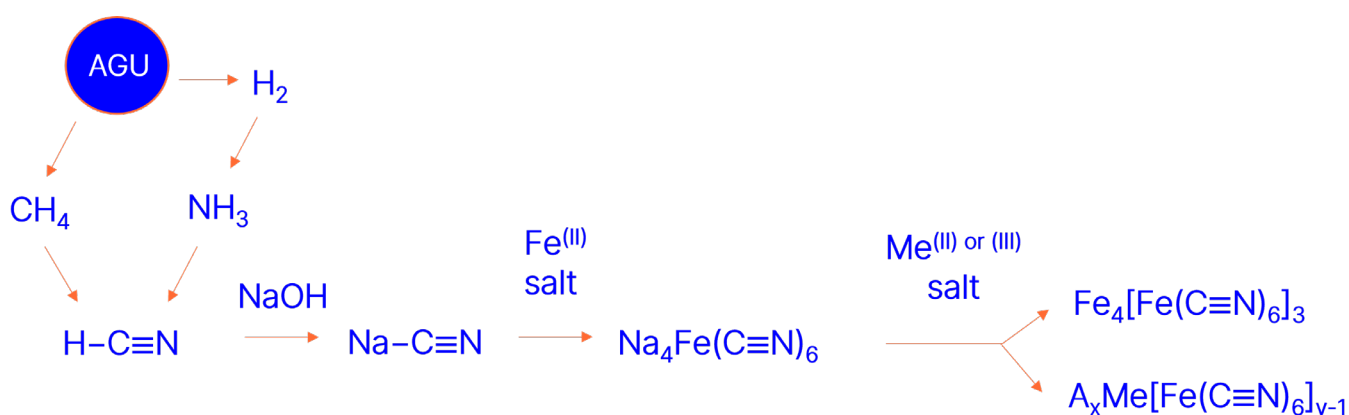
Battery cell's material components - anode, cathode, separator, and electrolyte - constitute the largest portion of the cell's cost. Particularly cathode materials are crucial for metal-ion batteries, as they dictate the battery's capacity and influence the overall energy/power densities and safety. PBAs are notable for their open and stable three-dimensional structures with large ion transport channels and lattice gaps, which enable efficient transport and storage of charge carriers. This makes them promising candidates for cathode active materials (CAMs) in rechargeable batteries, particularly in SIBs⁶. By changing the metal in the structure, the active site of PBAs and the corresponding redox potential can be modified, allowing for the adjustment of the output voltage of Prussian blue-type cathode materials⁷. Besides their application in commercial SIBs⁸, PBAs have also been studied for use in multivalent metal ions, such as magnesium or zinc, energy-dense batteries, improving the performance and cycle life of these systems⁶. Ferrocyanides, due to their high solubility and stable redox behavior have also been investigated for use in RFBs. Vanadium RFBs are well-established but have limitations, such as the high cost of vanadium, prompting the search for alternatives. Ferrocyanide-based compounds, particularly the ferro-/ferricyanide ($[\text{Fe}^{2+}(\text{CN})_6]^{4-}/[\text{Fe}^{3+}(\text{CN})_6]^{3-}$) redox couple have been explored as active redox species in various types of flow batteries, e.g. aqueous redox flow batteries (ARFBs)⁹⁻¹². Furthermore, the potential of PB-based materials for use as electrodes for supercapacitors and anodes for metal-ion systems including LIBs, due to their unique structural properties and large surface area, have been demonstrated¹³⁻¹⁵.

The synthesis methods for PBAs vary across several key parameters, significantly influencing the structure and electrochemical performance of the resulting materials. PBAs exhibit considerable structural variation, which directly impacts their electrochemical properties. Typically, PBAs are synthesized through the co-precipitation of a metal salt and a hexacyanoferrate complex. Factors such as the concentration and oxidation state of the precursors, flow rate, temperature, and additional salts can all potentially alter the structure of the final product¹⁶.

Arxada is well-equipped with its cyanide operations and extensive experience in the industrial manufacturing of battery grade materials

The Visp's cracker (Acetylene Generating Unit, AGU) continuously produces several streams of essential base chemicals, including acetylene, ethylene, and methane. Methane serves as feedstock for the cyanide unit, where it is converted into hydrogen cyanide (HCN), which can then be used to produce PB and its analogues. In addition to our backward-integrated operations, we offer proven expertise in scaling up battery-grade PB or PBAs materials and customizable, tailor-made CDMO solutions (Figure 2).

Figure 2: Schematic illustration of Arxada's cyanide operations and its integration into the chemical network in Visp. "A" in the PBAs general formula stands for insertion, alkali metal, ion; "Me" stands for metal.



Continued growth of battery energy storage market, technological advances and other factors such as cost, production scalability, and sustainability open a path for novel chemistries. Ferrocyanides, such as PBAs are carving a niche as materials for cost-effective, large-scale energy storage systems, leveraging their compatibility with SIBs. PBAs offer low cost, high stability, and good theoretical capacity. While the electrochemical properties of PBAs can be limited by factors such as particle size, morphology and crystallinity, their low cost and the possibility of being tailored in composition and framework to meet various battery application requirements remain attractive attributes¹⁷. By optimizing material performance and improving production processes, PB-based battery materials may play a significant role in the development of the new energy industry.

Summary

Ferrocyanides and their derivatives, particularly PBAs, are emerging as promising candidates in various energy storage applications, as they are specifically valuable for their affordability and electrochemical performance. These applications include:

- Sodium-ion batteries, where they provide a promising performance used mainly as cathode active materials
- Redox flow and energy-dense flow batteries, used as electroactive components, where their high solubility and long-term stability are beneficial for stable cycling performance and large-scale, cost-effective energy storage
- Alternative metal-ion batteries, where their ability to intercalate various ions provides a promising avenue for more sustainable and high-capacity energy storage solutions
- Supercapacitors, where their excellent conductivity and charge storage capabilities make them suitable for high-power density applications

Arxada's team looks forward to the ongoing development and advances of energy storage technologies and is ready to offer services and expertise in scaling up production of materials including ferrocyanides for energy storage applications.

Our offer

- **Proven track-record and decade-long backward integrated cyanide operations**
- **Experience with development and manufacturing of Prussian Blue and other high performing battery grade materials**
- **Fully integrated CDMO services tailored to customers' aspirations and afflictions**
- **Provide solutions to achieve a short time-to-market for your battery scale-up and large-scale production**
- **Focus on what matters to you.**

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