

A New Solid-State Sodium-Metal Battery

Samuel Wheeler, Kevin Hurlbutt, Mauro Pasta*

Department of Materials, University of Oxford
Oxford, OX1 3PH, UK

Summary

Sodium batteries and solid-state electrolytes are two research directions in the effort to develop electrochemical energy storage that goes beyond lithium-ion. In this issue of *Chem*, Goodenough *et al*¹ combine a sodium-metal anode, a NASICON solid electrolyte, and a Prussian blue analogue cathode for an energy-dense, long-lived battery.

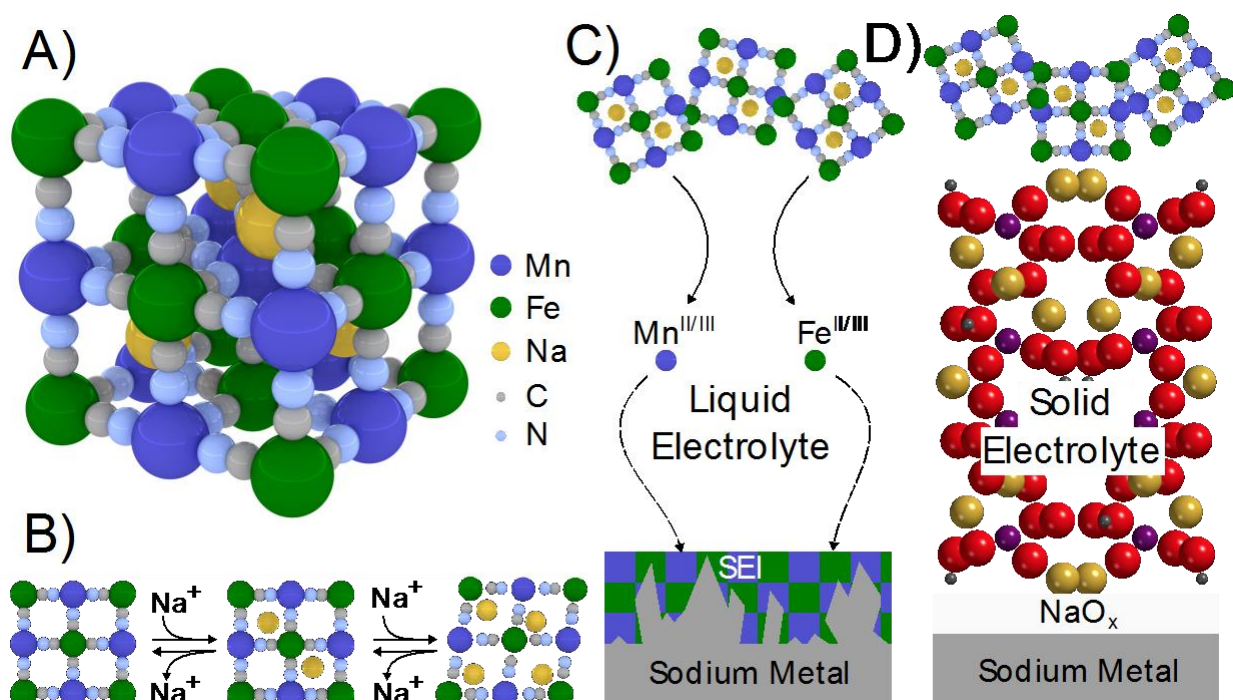


Figure 1. Prussian blue analogues have a face-centered, cubic geometry. (A) Half the interstitial cages are occupied by sodium ions. (B) A cubic-rhombohedral transition is often seen in PBA materials when the insertion ion content exceeds a critical value. (C) In a liquid organic electrolyte, the active material in the cathode is susceptible to dissolution into the electrolyte. Goodenough *et al* found manganese and iron in the solid-electrolyte interphase as well as significant dendrite growth. These phenomena lead to rapid capacity fade. (D) A solid NASICON electrolyte prevents dissolution of the cathode and suppresses dendrite formation for improved cycle life.

Electrical energy from renewable sources, notably wind and solar, are inherently intermittent and unpredictable. Strategies and technologies must, therefore, be developed to ensure that energy supply and demand are matched on time scales ranging from seconds to days. One such strategy is using grid-scale energy storage the critical performance metrics of which are cost, cycle life, and calendar life, in contrast to energy density, which is key in portable electronics.² Economies of scale and decades of optimization have driven down the cost of lithium-ion batteries, but there are concerns around the further increase in lithium price. In contrast, sodium's abundance gives it a lower cost as a raw material, and its

ubiquity ensures stability of that cost over time. Moreover, a sodium-based chemistry allows for the substitution of the costly and heavy copper current collector with inexpensive and lighter aluminum.³ Additionally, the transition metals used to make cathodes in current lithium-ion batteries are expensive, and the overall cycle life of these systems are likely inadequate for grid-scale storage. One family of candidate materials for cathodes in sodium batteries are comprised of inexpensive and readily available raw materials and have been shown to operate reversibly for tens of thousands of deep discharge cycles: Prussian blue analogues (PBAs).⁴

Prussian blue is the prototype of PBAs, which share a common crystal structure but span a range of compositions. They contain two transition metal ions, bridging cyanide ligands, and interstices accommodating inserting ions. The transition metals are ordered in a fcc arrangement; one is octahedrally coordinated to carbon atoms, and the other is coordinated to nitrogen atoms (**Figure 1A**). The general formula is $A_xP[R(CN)_6]_{1-y} \cdot \square_y \cdot wH_2O$ where P and R are transition metals, A is an interstitial ion species, and \square represents a hexacyanometallate vacancy. Vacancies and water content strongly affect the material's stability and ionic conductivity.⁵ The open-framework structure allows for the insertion of a range of alkali and alkaline earth cations with excellent kinetics and minimal change to the framework itself; this leads to the long cycle life discussed above.

Hexacyanoferrates with iron at the carbon-coordinated position have redox potentials between 3.0 and 3.8 V versus Na^+/Na , making them ideal cathode materials. To reach their maximum theoretical specific capacity, around 170 mA h g^{-1} , both transition metals must be electrochemically active within the relevant potential range.⁶ This allows a two-electron reaction per formula unit and full utilization of interstitial ion sites in the structure (**Figure 1B**). In addition, to maximize the capacity, the hexacyanoferrate vacancy content must be minimized. Thorough research into hexacyanoferrates have identified three analogues in which the nitrogen-coordinated ion is electrochemically active: hexacyanoferrates of iron,⁷ manganese,⁸ and cobalt.⁹ The price of cobalt is high and increasing. This leaves manganese and iron hexacyanoferrate as primary candidates for cathode materials in low-cost grid-scale batteries. Of the two, manganese hexacyanoferrate has a higher average discharge potential for a higher energy density.

However, it does suffer from a limited cycle life which is caused by three phenomena. First, on oxidation to Mn^{3+} , a Jahn-Teller distortion of the MnN_6 octahedra deforms the crystal structure and decreases reversibility.¹⁰ The second is the disproportionation reaction of Mn^{3+} into Mn^{2+} and Mn^{4+} that can accelerate the dissolution into the liquid organic electrolyte, leading to side reactions and irreversible capacity loss. Finally, manganese catalyzes the decomposition of the electrolyte forming corrosive species that further accelerate the cathode dissolution.

In this issue, Goodenough *et al*¹ tackle these problems for a manganese hexacyanoferrate cathode by replacing the organic liquid electrolyte (**Figure 1C**) with a solid NASICON electrolyte (**Figure 1D**). Simultaneously, the solid electrolyte enables the use a sodium-metal anode, which has high specific capacity ($1,166 \text{ mA h g}^{-1}$) and low redox potential (-2.7 V versus SHE). Direct comparison between the cells containing the solid electrolyte and conventional organic electrolyte are presented.

Cells using an organic electrolyte show very poor cycle life and considerable capacity fade over the first 200 cycles, although the group has previously achieved significantly better performance with the same cathode in a different organic electrolyte.⁸ In contrast, cells using the solid electrolyte show significantly slower capacity fade. As seen through *ex situ* XRD, the diffraction pattern of the cathode is maintained after cycling using a solid electrolyte. The intensities of XRD reflections decrease significantly, however, after cycling with the organic electrolyte. They propose that decomposition of the organic electrolyte, potentially catalyzed by the PBA active material itself, produces reactive species such as hydrogen fluoride and water. These species then attack the PBA active material accelerating its dissolution. On the other hand, their NASICON solid electrolyte is not susceptible to oxidative decomposition.

They analyze the electrode surfaces after cycling to investigate the composition of the SEI and shine light on the decomposition processes. X-ray photoelectron spectroscopy of the surfaces of both electrodes cycled in organic electrolyte shows the presence of numerous chemical species, including oxides and fluorides of iron, manganese, and sodium. In cells cycled with the NASICON electrolyte, sodium oxide and organic molecules are present on the cathode surface. Only sodium oxide is detected on the anode, although some products could have been lost during sample preparation. SEM images of the two surfaces show that the solid electrolyte inhibits the formation of sodium dendrites compared to the organic electrolyte.

To ensure adequate ionic conductivity of the solid electrolyte the NASICON cells were operated at 60°C. This elevated temperature affects the mechanical properties of sodium metal and, therefore, its propensity to form dendrites, as well as the wettability at the interface. Additionally, this is relatively close to the melting point of sodium (97.8°C) thus limiting the feasible operating temperature range.

This work introduces, for the first time, a full cell that incorporates a PBA cathode with a solid electrolyte. Eliminating the organic electrolyte suppresses dissolution of the active material for an improved cycle and calendar life. The solid electrolyte inhibits dendrite growth to enable a sodium-metal anode with substantially higher specific capacity. With scalable methods of solid-state battery manufacturing, the work presented here can lead to a low-cost, long-lived battery suitable for use in grid-scale energy storage.

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