Sandia National Laboratories

SAND2019-8391D

Tunable Electrical Conductivity of Thin Films of Prussian Blue

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Background

Research into materials with readily tunable conductivity can improve sensors, semiconductors, low power electronics, flexible electronics, reconfigurable electronics, and neuromorphic computing. However, current materials such as PEI-doped PEDOT:PSS have shorter stability and are more difficult to synthesize.

Prussian blue (PB), a porous mixed-valence polynuclear transition metal cyanide complex, not only overcomes the previous two challenges but exhibits two properties pertinent to this project: (1) its electrochromic behavior (**Figure 1**) and (2) its high speed proton conductivity (**Figure 2**). This implies that the conductivity is not only tunable but capable of fast on-chip tunability leading to better performance than PEI-doped PEDOT:PSS.

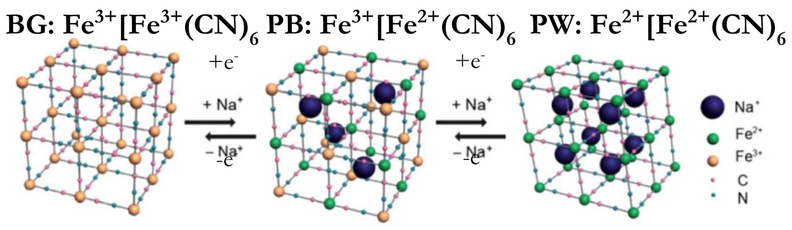


Figure 1. Schematic of the redox behavior of PB. Prussian White (PW) is the reduced form of PB, while the oxidized form is Berlin green (BG). Figure adapted from Wu et al. *Sci. Adv.* **2017**, *3, 12*

Importantly, PB generally exhibits insulating behavior, while Prussian White (PW) and Berlin Green (BG) have increased electrical conductivity. Thus, we hypothesize that semi-reduced or semi-oxidized forms of PB will have variable electrical conductivity as a function of oxidation state.

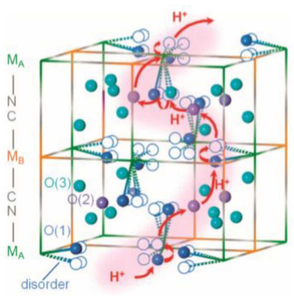


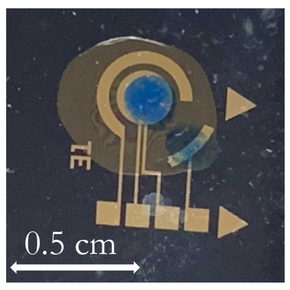
Figure 2. Grotthuss proton conduction in PB structure. Adapted figure from Ohkoshi *et al. J. Am. Chem. Soc.* **2010**, *1321*, 96620-6621.

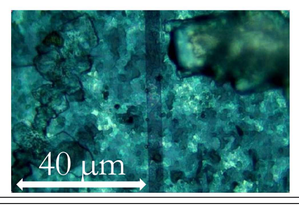
These reactions are accompanied by mass transfer of alkali metal ions in aqueous solution to charge balance. PB is capable of fast proton conductivity via an interstitial hydrogen bond network in the hydrated material. This is known as the Grotthuss proton conduction mechanism (Figure 2). Thus, we surmise that the material is capable of high speed switching by using free protons as counter ions as the material undergoes redox chemistry.

Therefore, our project goals are to: (i) investigate the tunability of the electrical conductivity of PB, and (ii) to create prototype PB-based devices.

Deposition Method

Colloid precursor solution (Chen *et al. Colloid J.* **2007**, *69*, 660–665**):** 2 mM $K_4[Fe(CN)]_6$ was mixed with 0.1 M KCl in 10 mM HCl. Subsequently, 2 mM $FeCl_3$ was added dropwise into the $K_4[Fe(CN)]_6$ solution under vigorous stirring. A blue solution was gradually formed, and the reaction was completed overnight. The obtained colloid solution was stable for three weeks.



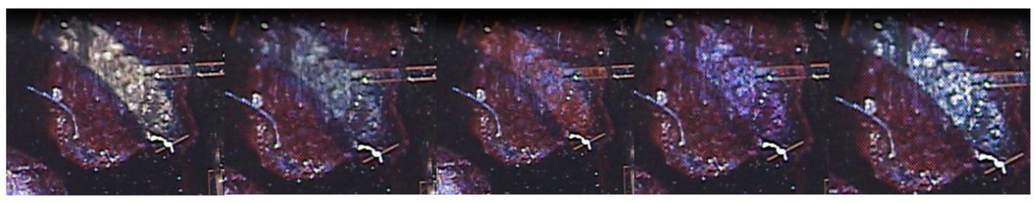


This image shows a completed prototype device fabricated on a generic metal oxide test platform (GMOP). This is a silicon chip with vapor deposited Pt electrodes. Precursor solution was drop cast (10 layers) selectively to bridge the central source and drain electrodes and to grow on the gate electrode. Drop cast Nafion (1 layer) bridges the deposited PB.

This microscope image shows the deposited PB clearly bridging the source/drain channel. The film itself is fairly thick but not very uniform.

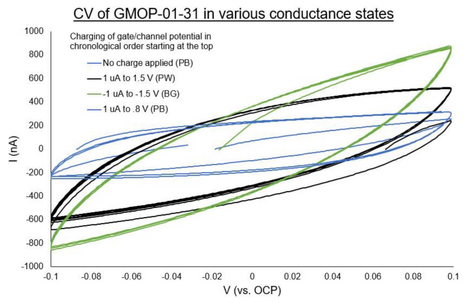
Electrical Data

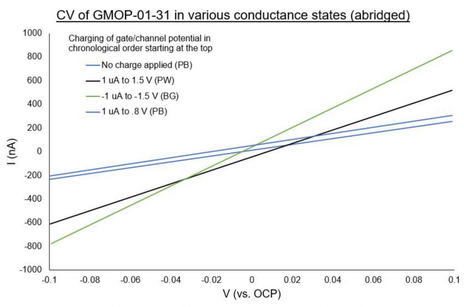
Images of GMOP-01-31 gate at various gate/channel potentials



1.5V .8V none -.8V -1.5V

The gate electrode transitions from PW to PB to BG, as various gate/channel potentials are reached.

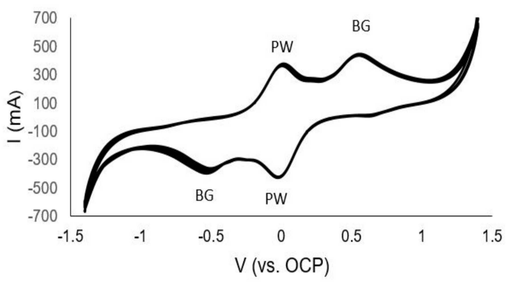




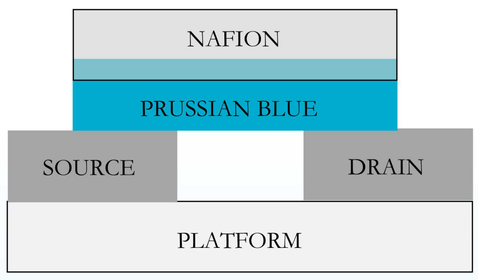
Electrical data of source/drain current supports that there are distinct conductance states. Three were isolated with their respective source/drain CV data above. It was possible to switch back and forth between them.

Preliminary Cyclic Voltammogram

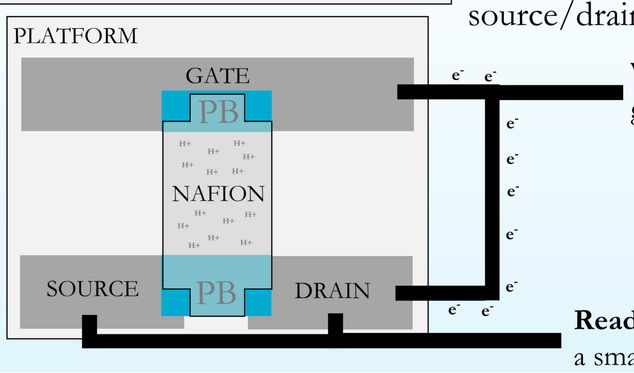
Two PB coated electrodes in aqueous electrolyte counter each other undergo the transition from PW to PB to BG. This data shows the capacity for two PB electrodes to engage in redox chemistry opposite each other, which is the basis for the solid state device architecture below.



Device Architecture



Metallic electrodes on an insulating platform are bridged by deposited Prussian blue. A layer of solid state electrolyte, Nafion, a polymer containing branched terminal sulfate groups, acts to extend the Grotthuss proton conduction pathway to allow ion exchange between the Prussian blue deposited on the isolated gate and source/drain electrodes.



Write: The device is charged by applying a gate/channel potential

Read: The state of the device is read by applying a small source/drain potential

Conclusion

PB exhibits tunable conductivity with a plethora of conductance states. Additionally, a prototype solid state memory device was successfully fabricated. However, there are two major problems with the system: (i) the ionic current overwhelms the electronic current resulting in high diffusion limited read times, and (ii) the hypothesized "hybrid states" of PB exist but are unstable without a constant current maintaining them. Overall, PB can be ruled out as a feasible material for use in high speed fine-tunable memory devices. However, there is an Ru-based analogue of PB, $K_{1.2}Ru_{3.6}[Ru(CN)_6]_3 \cdot 16H_2O$, which is 3 orders of magnitude more electronically conductive than PB (Behera *et al. Chem. Mater.* **2009**, *21*, 1922–1926). This material potentially alleviates the overwhelming ionic current.

Acknowledgements

Funding: Department of Energy Visiting Faculty Program
Sandia National Laboratories: Dr. Mark Allendorf
University of Michigan: Erik Isele
University of Florida: Carlos Casadevall