

Hope College

Hope College Digital Commons

19th Annual Celebration of Undergraduate
Research and Creative Activity (2020)

Celebration of Undergraduate Research and
Creative Activity

4-17-2020

Aqueous and Non-Aqueous Characterization of the Charge Storage of Prussian Blue Analogues with Varying Modification Procedures

Kameron Wilcox
Hope College

Follow this and additional works at: https://digitalcommons.hope.edu/curca_19

 Part of the [Physics Commons](#)

Recommended Citation

Repository citation: Wilcox, Kameron, "Aqueous and Non-Aqueous Characterization of the Charge Storage of Prussian Blue Analogues with Varying Modification Procedures" (2020). *19th Annual Celebration of Undergraduate Research and Creative Activity (2020)*. Paper 6.

https://digitalcommons.hope.edu/curca_19/6

April 17, 2020. Copyright © 2020 Hope College, Holland, Michigan.

This Poster is brought to you for free and open access by the Celebration of Undergraduate Research and Creative Activity at Hope College Digital Commons. It has been accepted for inclusion in 19th Annual Celebration of Undergraduate Research and Creative Activity (2020) by an authorized administrator of Hope College Digital Commons. For more information, please contact digitalcommons@hope.edu.

Aqueous and Non-Aqueous Characterization of the Charge Storage of Prussian Blue Analogues with Varying Modification Procedures



Kameron E. Wilcox and Dr. Jennifer R. Hampton
Department of Physics, Hope College, Holland, MI 49423

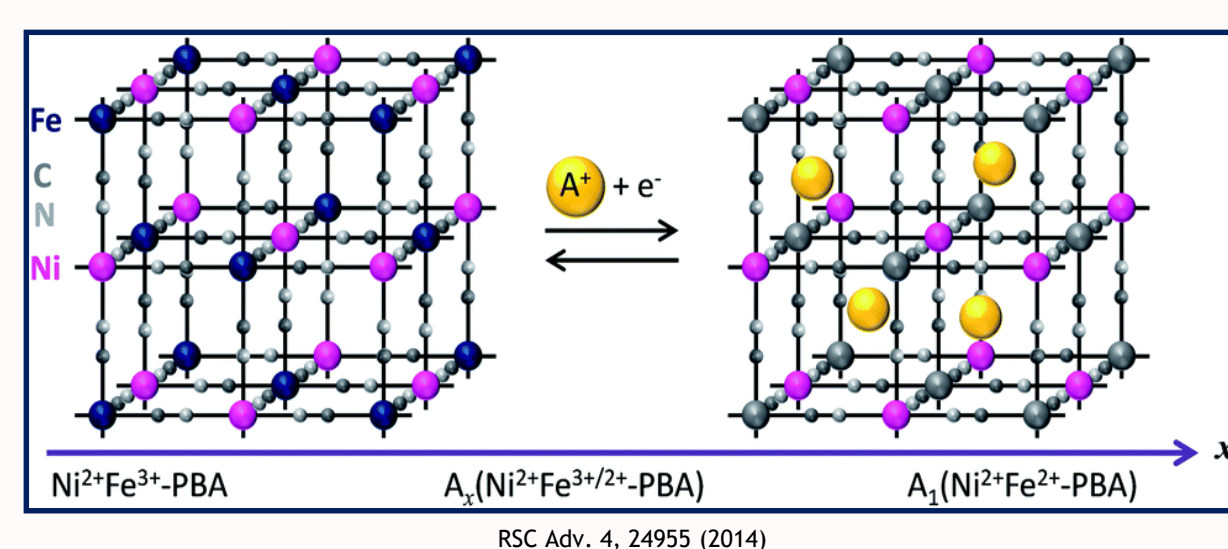


Abstract

Prussian Blue analogues (PBAs) provide a promising look into the future of battery materials; their low cost and facile creation grants the opportunity for a commercially viable battery. In addition, their components consist of earth-abundant elements, which may potentially lead to a green battery material, an area of growing importance to the majority of people today. The modification process in which the PBA forms may be carried out by one of two techniques: the standard CV technique consists of performing cyclic voltammetry in a modification solution for a set number of cycles, and the dipping technique involves submerging the substrate in the solution for a specific amount of time. In order to better understand the time dependence of spontaneous PBA formation, substrates were dipped in modification solution for varying amounts of time ranging from 15 seconds to 600 seconds. Additionally, hydrolysis is believed to occur and affect charge storage measurements during characterization. To better understand the effect of hydrolysis on characterization measurements, some samples were characterized with .1 M NaClO₄ in both an aqueous solution and a non-aqueous, acetonitrile-solvent (CH₃CN) solution. Comparisons between the data from both characterizations may lead to a better understanding and accounting of the effects of water when characterizing aqueously.

Prussian Blue Analogues

Prussian Blue Analogues are open-framework intercalation compounds with properties suitable for energy storage and charge transport. For nickel hexacyanoferrate (NiHCF) the nitrogen-coordinated sites are occupied by Ni²⁺. The reaction below uses A to represent Na. Running a current through the PBAs allows us to calculate the total possible charge held by the sample. By doing so, we can understand how varying the production of NiHCF in modification affects the formation of PBAs.



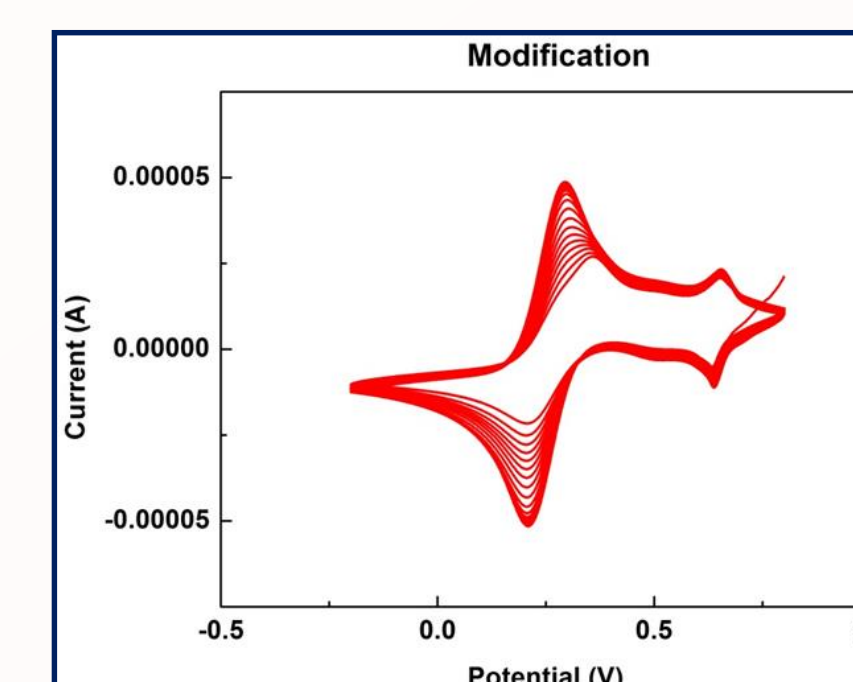
Modification

Modification is the step of producing the PBA on a nickel film. A modification solution consisting of 1 M NaNO₃ and .01 M K₃Fe(CN)₆ provides the chemicals required to create the PBA. This step can be performed by one of two methods: dipping and cyclic voltammetry (CV).

Dipping was performed on gold samples with time in solution being the independent variable. The effect of dip time on total oxidation charge storage was studied at values of 15s, 30s, 60s, 120s, 300s, and 600s.

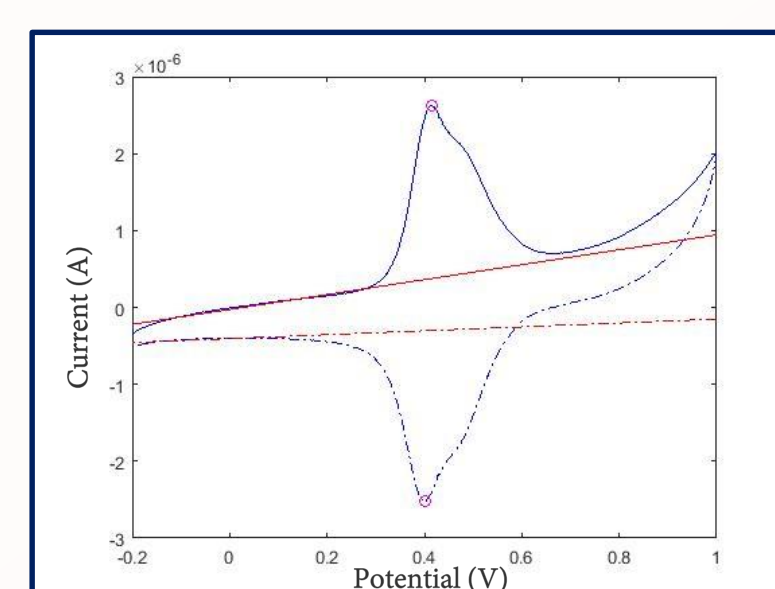
Cyclic voltammetry was performed on indium tin oxide (ITO) samples for 30 cycles at 50 mV/s.

Right: An example cyclic voltammogram created during CV modification.



Characterization

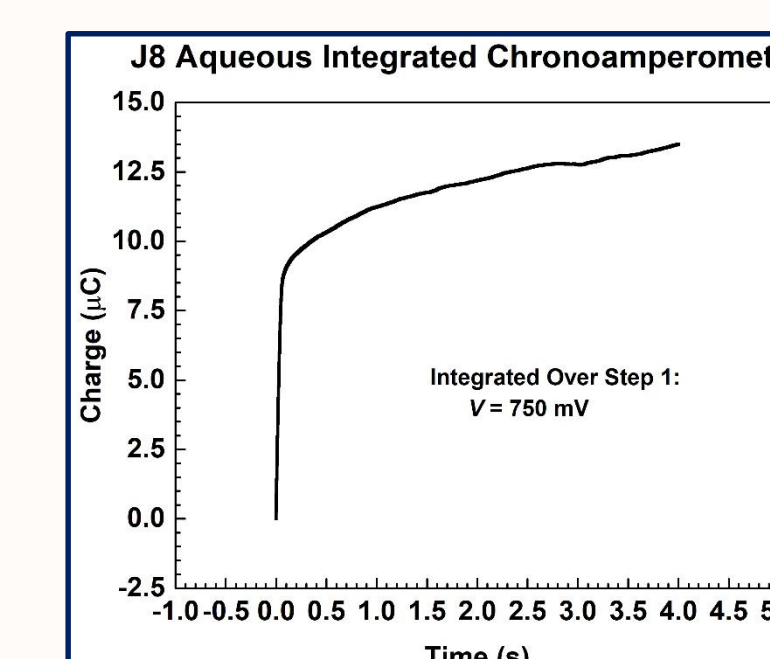
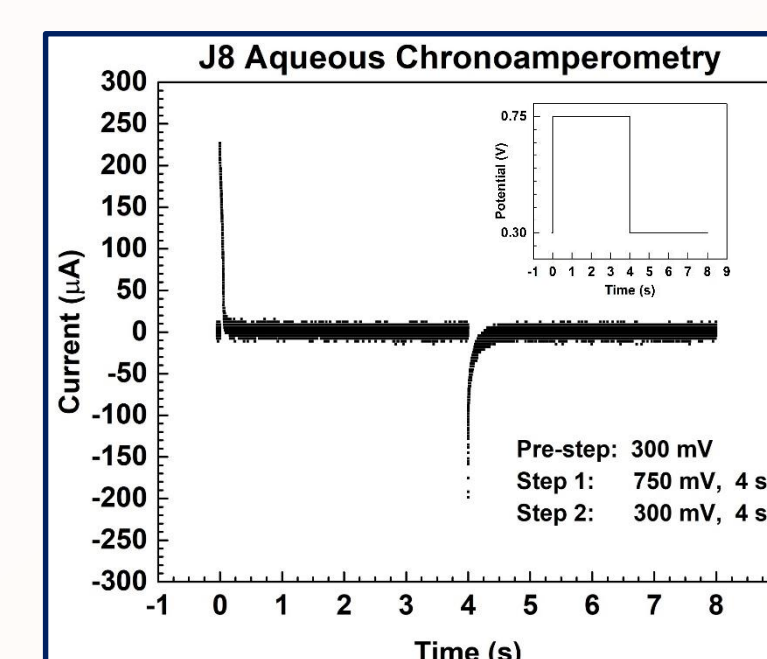
Depending on the test being performed, characterization consists of one or two steps. Regardless of the test, characterization always consists of studying charge storage through cyclic voltammetry in which the potential changes at a constant rate. However, when studying aqueous and non-aqueous characterizations, chronoamperometry is also performed in which the potential changes according to a step function. In both cases the current is measured, and the only difference is how the potential changes.



Left: A cyclic voltammogram formed at a scan rate of $\frac{dV}{dt} = 50 \frac{mV}{s}$.

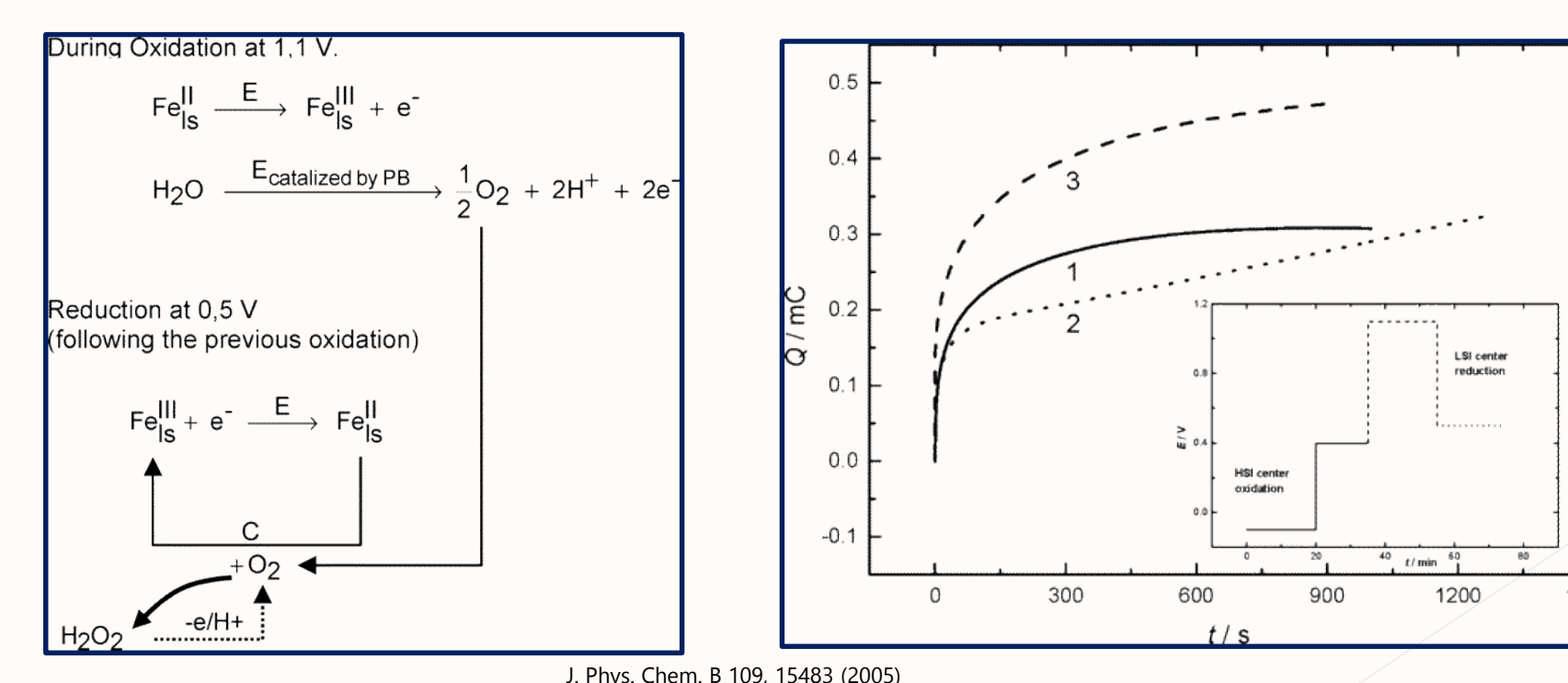
Right: A current vs. time graph created during chronoamperometry.

Far Right: A charge vs. time graph attained through integration of the current vs. time graph from chronoamperometry.



Aqueous vs. Non-Aqueous

At higher potentials of cyclic voltammetry in aqueous solutions, an increase in current is seen. Orellana et al. explain this phenomenon to be the oxidative hydrolysis of water catalyzed by Prussian blue. Under ideal conditions, the charge would approach a maximum value as the PBA becomes fully charged during chronoamperometry; however, a linear increase in charge is observed to emerge at later times. Orellana et al. also claim that this linear increase in charge can be described as a result of the catalysis. In order to test that we are observing this catalysis in our CVs, chronoamperometry is being studied on ITO samples in aqueous and non-aqueous solutions containing .1 M NaClO₄ at potentials of .4 V, .6 V, .75 V, and .9 V.



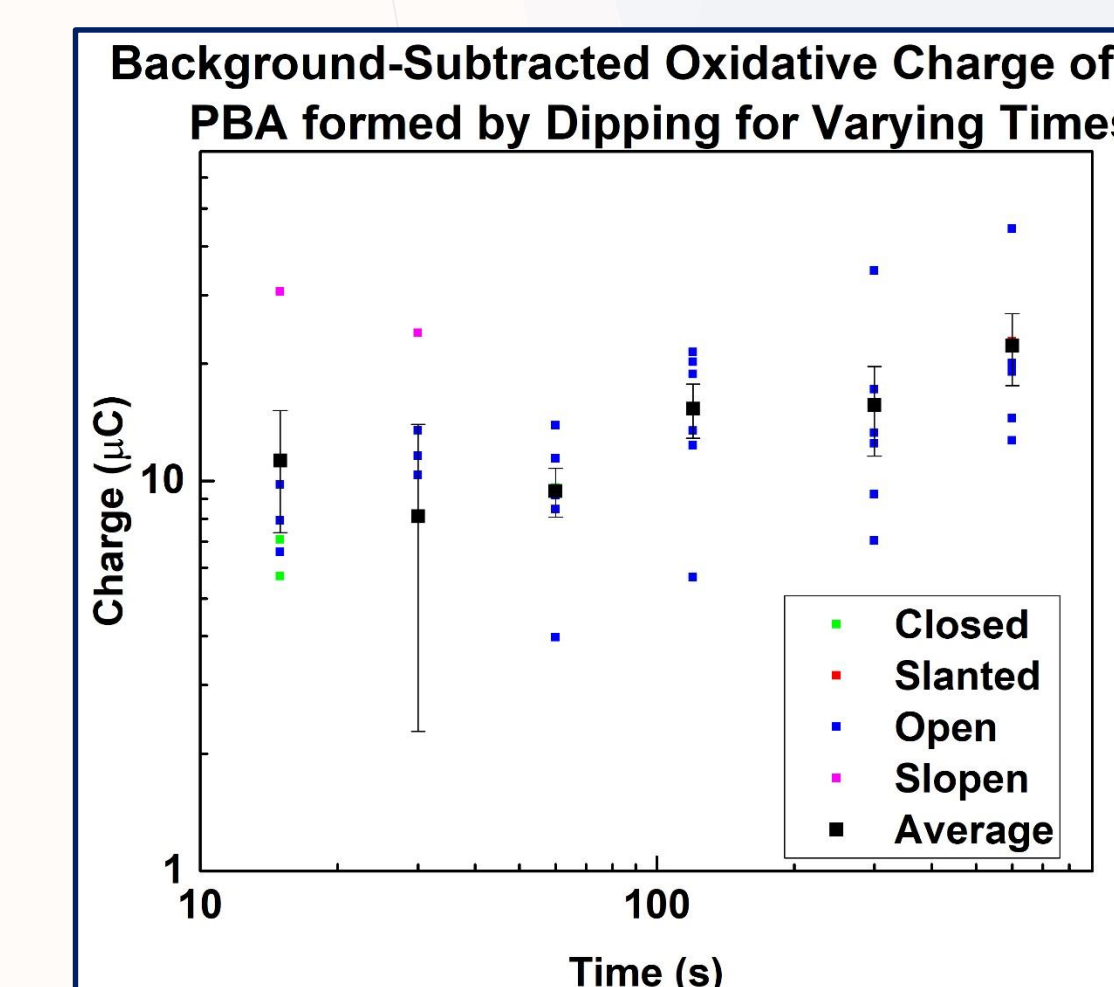
Above Left: The model of catalysis proposed by Orellana et al.

Above Right: Chronoamperograms modeling how catalysis affects chronoamperometry of Prussian blue.

Dipping Times

PBA will form spontaneously when nickel is dipped in the modification solution. The speed of this spontaneous formation is unknown, so in order to better understand this process, gold substrates were dipped in the modification solution for 15s, 30s, 60s, 120s, 300s, and 600s.

Below: The data collected to date within the dipping times test. While a trend appears, the uncertainties indicate that any trend is not significant. More data will be collected to reduce the size of the uncertainties.



Acknowledgements

The Hope College Surface Lab: Scott D. Joffre, Brittany T. Devlin, Jacob M. Kelley, and Forest D. Rulison.

The generous funding provided by the National Science Foundation under NSF-RUI Grant No. DMR-1608327, NSF-MRI/RUI Grant No. PHY-0319523, and NSF-MRI Grant No. CHE-0959282 made this research possible.

