XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry
Belo Horizonte, September 12 - 15th 2024

Synthesis and Electrochemical Analysis of Prussian Blue Analogs for Sustainable Energy Storage: Insights from CV and EQCM Technique Studies

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Thematic Area: Inorganic Electrochemistry

Keywords: Ionic Insertion Batteries, EQCM, Prussian Blue Analogs

Over the last years, the discussion about climate change and the necessity for new sustainable technologies has aroused scientists' interest in the development of new materials for applications in the energy field. Energy storage systems (ESSs), such as batteries utilized in everyday life, play a crucial role in ensuring energy supply and, in the coming years, may integrate more sustainable materials. Li-Ion batteries have the greatest attention for this energy supply due to their great performance and wide potential range. However, their use of organic electrolytes and the presence of heavy metals in their composition have prompted scientists to explore new materials for the batteries field. One of these materials is the Prussian Blue Analogs (PBAs), also known as Hexacyanoferrate (HCF). The HCF is interesting because of its structure, which is based on the general formula AxM[M'(CN)6)z.nH2O, where A is a mono or multivalent alkaline metal such H, K, Li, or Na responsible for the mechanism in ionic insertion, M denotes a transition metal like Cu, Co, Zn which offers different potential or catalytic properties and M' is Fe. The PBAs in literature have been applied in ionic insertion electrochemical systems. They had been studied in Aqueous Rechargeable Ion Batteries (ARIBs) systems based on aqueous electrolytes with less danger in manipulation and good performance. Many researchers have developed various PBA syntheses. However, there is a lack of understanding of its actual mechanism when applied in aqueous electrochemical systems. The Grotthus mechanism is one of the most acceptable ones. Based on that, this work had the goal of developing different thin films based on HCF materials in a Pt wire substrate, which were copper (CuHCF), vanadium (VHCF), zinc (ZnHCF), cobalt (COHCF) and manganese (MnHCF). From our own methodology electrodeposition synthesis, all thin HCF films were studied using Cyclic Voltammetry (CV) and Electrochemical Quartz Crystal Microbalance (EQCM). The EQCM technique is an important method based on the Sauerbrey Equation, which implies the exploration of a relation between frequency and mass oscillation due to deformation on a quartz crystal surface and in this work, it was used to quantify, understand, and propose the ionic mass transfer mechanism considering the Grotthus mechanism as possible a part of it. The synthesized HCF thin films were studied in a 4M H2SO4 medium. The analysis was made by CV with scan rates of 2 $mV.s^{-1}$, 5 $mV.s^{-1}$, 10 $mV.s^{-1,}$ and 20 $mV.s^{-1,}$ and the EQCM analysis was also considered for these CV scans. However, 5 $mV.s^{-1}$ has demonstrated a better stable behavior for mass and species involved in charge transfer calculus, with an average mass variation of 25 $µg.cm^{-2}$. The work proposed that proton and hydronium ions could both participate in ion exchange due to the open cubic framework of PBAs, which allows the free movement of these species due to the medium used for this research.

Acknowledgments: This work was funded by the CNPq organization.

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