

Cation effect on Prussian blue and analogues electrodeposition: structure, stability and application as electrodes for batteries.

Samantha Husmann^{1*} (PG), Aldo J. G. Zarbin¹ (PQ)

¹ Grupo de Química de Materiais (GQM), Universidade Federal do Paraná (UFPR) – Curitiba, PR

* samanthahus@gmail.com

Palavras Chave: Prussian Blue, carbon nanotubes, cation, battery, thin films.

Abstract

The structure and properties of Prussian blue and analogues electrodeposited with different cations were evaluated.

Introduction

Prussian blue (PB) and its analogues (PBA) are complexes with general formula $AM'[M(CN)_6]$, with A being a counter cation, M' and M metal species coordinated with N and C, respectively. PB(A) present a porous face centered cubic structure and electrochemical properties that make them suitable for several applications, such as sensors and batteries. The performance of PB(A) is deeply related to their stability and size of the interstitial sites. Mainly, the size depends on metal species and defect degree, which in turn are influenced by the synthesis method and the cation used during PB(A) formation. PB(A) are known to present poor chemical and electrochemical stability, that can be improved by processing them as composites. Our group developed a route to synthesize transparent films of carbon nanotubes (CNTs)/PB(A) composites that are highly stable, presenting good performances as sensors and electrochromic materials.^{1,2} In these routes, PB(A) are synthesized with KCl as supporting electrolyte (SE). Seeking new properties and aiming better performance of the materials, CNT/PB(A) films were synthesized using NaCl and LiCl as SE. The stability and structure of the composites were evaluated by cyclic voltammetry, XRD, Raman spectroscopy and SEM. The effect of the different structures in the application of the films as electrodes for battery was also verified.

Results and Discussion

CNTs thin films were prepared by interfacial method, using Fe- or Co-filled CNTs, according the methodology developed in our group.^{3,4} Electrodeposition of PB, ruthenium purple (RP) and cobalthexacyanoferrate (CoHCFe) was done by cyclic voltammetry (CV) at optimized conditions. Three different SE were used during deposition, KCl, NaCl and LiCl 0.1 mol L⁻¹, generating nine different composites (CNT/PB(A)K, CNT/PB(A)Na and CNT/PB(A)Li). Voltammetric profiles of the species electrodeposited under different SE presented very different redox potentials. The electrochemical stability of CNTs/PB(A) films were evaluated by CV

in the three electrolytes. Among PB films, only the one electrodeposited within KCl (CNT/PBK) presented good stability in KCl. Both CNT/PBNa and CNT/PBLi lost almost 100% of initial signal and all three films showed poor stability in NaCl and LiCl. Between RP films, a slightly improve in the stability in NaCl was observed for the CNT/PRNa and CNT/PRLi films, although none of them presented stability in LiCl. The most interesting behavior was observed for the CoHCFe films, in which the cation had more pronounced effect in the structure and stability of the material. CNT/CoHCFeNa presented great stability at all three electrolytes, showing the ability to be cycled in more than one electrolyte repeatedly and retain its electrochemical response. The modifications in the structure of PB(A) formed with different cations could be observed by peak shifts and enlargements at XRD. These changes were also evaluated by SEM images, which showed the dependence of the cubic nanoparticles size with the nature of the cation. Raman spectroscopy showed the interaction between CNT and PB(A), that is strictly related to the electrochemical stability observed for the films. The cation effect on structure and stability of the materials also affected their performances as battery electrode. Composites with more open or defective structures, obtained with larger ions (Na⁺ and Li⁺), had great improvement in battery capacity, showing more than 50% enhancement compared to K⁺ cycled films. Amongst all composites, CNT/CoHCFeNa presented the best results, with capacities around 175 mAh g⁻¹ and 95% stability during 2x10³ charge/discharge cycles.

Conclusions

The cation used for PB(A) electrodeposition affected their structure and stability by changing lattice size and interaction with CNTs. These properties improved their performance as battery electrodes, showing high capacities and great charge/discharge stability.

Acknowledgments

CAPES, CNPq, INCT-Nanocarbono, NENNAM (Pronex/Fundação Araucária/CNPq)

¹Nossol, E.; Zarbin, A. J. G., *Adv. Funct. Mater.* **2009**, *19*, 3980.

²Husmann, S.; Zarbin, A. J. G., *Dalton Trans.* **2015**, *44*, 5985.

³Salvatierra, R. V.; Oliveira, M. M.; Zarbin, A. J. G., *Chem. Mater.* **2010**, *22*, 5222.

⁴Schnitzler, M. C.; Oliveira, M. M.; Ugarte, D.; Zarbin, A. J. G., *Chem. Phys. Lett.* **2003**, *381*, 541.