Electroanalytical study of isoniazid oxidation on Ni and Co nanoparticles modified FTO electrodes

Martins, P.R.; Ferreira, L.M.C; Araki, K.; Angnes, L.
Universidade de São Paulo
Av. Prof. Lineu Prestes, 748, Butantã, São Paulo, SP, Brasil

Introduction

In the last years nickel hydroxide has been intensively used as electrode material to develop batteries anodes, electrochromic devices and chemical sensors[1-3]. It can be found in two forms at reduced state (alpha and beta phase). Recently Martins et al.[4] used the modified Tower method to synthesize pure nanostructured α-$Ni(OH)_2$, $Co(OH)_2$ and mixtures containing different proportions of nickel and cobalt (75:25 and 50:50), allowing materials that remains with the alpha phase even after 700 redox cycles.

In this work, we explore the potential of these materials to construct sensors for isoniazid determination by cyclic voltammetry and by amperomety/BIA (Batch Injection Analysis) using as electrode material α-$Ni(OH)_2$, α-$NiCo(OH)_2$ at proportions 75:25, 50:50 and $Co(OH)_2$, here denoted respectively Ni-100%, Ni-75%, Ni-50% and Co-100%.

Material and Methods

The Ni-100%, Ni-75%, Ni-50% and Co-100% were synthesized using a modified Tower method, as previously related[4]. Ciclovoltammetric and amperometric experiments were performed using a potentiostat μ-Autolab type III. For electrochemical Impedance Spectroscopy (EIS) was used a potentiostat/galvanostat Autolab PGSTAT 30 containing impedance module.

Batch injection analysis experiments were carried out using a homemade electrochemical cell adapted for FTO electrode. Injections of the standard solutions were performed using a motorized electronic micropipette EDP Plus EP-100.

The films of nanostructured materials were prepared under FTO (fluorine doped tin oxide) previously cleaned with isopropyl alcohol. Isoniazid stock solution was prepared dissolving 34.28 mg of the solid in 1 mol/L KOH electrolyte solution just before use.

Results and Discussions

Studies of EIS of the Ni-100%, 75%, 50% and Co-100% electrodes, in the presence of 2.0 mmol/L $Fe^{II}(CN)_6/Fe^{III}(CN)_6$ solutions and using a frequency in the range 1 MHz – 1 Hz, shows that the resistance for electronic transference decreased with increasing of amount Co at electrodes.

The cyclic voltammograms were recorded in the range -0.15 to +0.5 V in alkaline medium KOH 1 mol/L in the presence and absence of isoniazid. It was observed that the E_{ap} relative to the redox process $Ni^{II/III}$ was shifted cathodically when the amount of Co increased into materials. Thus the Ni-100%, 75% and 50% presented respectively an E_{ap} at +0.37, +0.33 and +0.29 V, the Co-100% presented an Eap at +0.42 V relative to the redox process $Co^{III/IV}$. In the presence of increasing concentrations of isoniazid was observed an oxidation wave localized at +0.075, +0.35, +0.29 and +0.39 V, respectively to Ni-100%, 75%, 50% and Co-100%.

It only was observed to Ni-100% a big shift in the oxidation potential of isoniazid. It shifted about of 0.29 V in relation of E_{ap} relative to redox process $Ni^{II/III}$. On the sensors with Ni-75%, Ni-50% and Co-100% the E oxidation of isoniazid is coincident with E_{ap} of $Ni^{II/III}$ and $Co^{III/IV}$.

The results for BIA-amperometric assays were consistent with the ones obtained using cyclic voltammetry. Figure 1 illustrates the BIA-amperometric response for injections of isoniazid using the Ni-75% modified electrode in strong alkaline media.

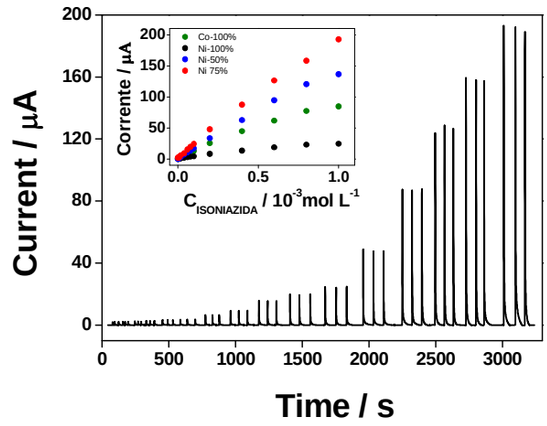

Figure 1: BIA-amperometric response for Ni-75% modified FTO electrode after injections of increasing concentrations of isoniazid solutions (from $1.0x10^{-6}$ to $1.0x10^{-3}$ mol L^{-1}). Inset: Calibration plots for the four different electrodes explored. The applied potential for measurements varies according with the optimal conditions for each electrode.

Repetition of alternating injections of 1.0 x 10^{-5} and 1.0 x 10^{-6} mol L^{-1} isoniazid solutions (not shown in Figure 1) resulted in a very good accuracy of current peaks and relative standard deviations less than 5% in all tested electrodes. The results demonstrate there is no memory effect between the alternating injections.

Another point to be highlighted is the high sensitivity achieved for isoniazid quantification utilizing the Ni-75% electrode in comparison with to other ones. In fact, the sensibility increases about 5.5 times for isoniazid detection in comparison with the Ni-100% modified electrode, presenting the lowest detection limit of 3.4 x 10^{-7} mol L^{-1}. Even being less sensitive, electrodes modified with α-$Ni(OH)_2$ present the advantage of be able to detect isoniazid in a much lower potential, condition which can avoid interferences in real samples.

Conclusions

The results here obtained demonstrated the potentiality of Ni-Co nanoparticles modified FTO electrodes associated with batch injection analysis and amperometric detection for quantification of isoniazid. The good accuracy provided by amperometry combined with this association makes it very suitable for analytical uses.

References

[1] H. Inoue, Y. Namba, E. Higuchi, *J. Power Sources*, 195 (2010) 6239
[2] M. Jafarian, M.G. Mahjani, M.G. Heli, F. Gobal and M. Heydarpoor, *Electroch. Comm.*, 5 (2003) 184.
[3] P.R. Martins, M.A. Rocha, L. Angnes, H.E. Toma and K. Araki, *Electroanalysis*, 23 (2011) 2541.
[4] P.R. Martins, M.A. Rocha, A.A. Parussolo, S.H. Toma, H.E. Toma and K. Araki, *J.Power Souces*, 218 (2012) 1.

Acknowledgments

CNPq, FAPESP