Electrochemical and X-Ray Absorption Spectroscopy Studies of Cobalt Coatings on a Hydrogen Storage Alloy

Renato C. Ambrosio and Edson A. Ticianelli

Instituto de Química de São Carlos – USP
C. P. 780, CEP 13560-970 São Carlos, SP, Brazil.
E-mail: edsont@iqsc.usp.br

This work reports the results of a study on the effect of electroless surface deposition of Co on physical and electrochemical properties of a metal hydride alloy. Electrochemical studies included measurements of charge/discharge polarization characteristics and the cycle life. X-ray absorption spectroscopy has been used to study the electronic properties of Co and Ni in the alloys, and X-ray diffraction to obtain the unit cell lattice parameters.

The Co deposition (20 wt. %) was carried out on the $LaNi_{4.7}Sn_{0.3}$ alloy powder using the procedure described in the literature [1]. X-ray diffraction (XRD) patterns had confirmed the hexagonal $CaCu_5$-type structure of the as cast alloy. Cycle-life tests were conducted in a three-electrode cell in 6 mol L^{-1} KOH, with a Pt mesh counter electrode and an Hg/HgO-KOH 6.0 mol L^{-1} reference electrode. The electrodes were discharged down to the cutoff potentials of – 0.70 V and – 0.80 V. X-ray absorption data were collected in the transmission mode, with the ionization chambers filled with air, in the K edge of Ni and Co. XANES and EXAFS spectra were analyzed using the WinXAS software, as described elsewhere [2].

Figure 1 shows typical discharge profiles at the 10^{th} cycle, obtained for the $LaNi_{4.7}Sn_{0.3}$ alloy with and without the surface treatment. For the cobalt-plated alloy, two plateaus are observed in the discharge profiles. This behavior is characteristic of electrodes onto which two successive reactions are occurring. The first plateau located at less anodic potentials is attributed to the well-characterized process of the hydride oxidation (hydrogen oxidation reaction - HOR) [2], while the second must be due to some surface process related to the Co layer [1]. This result indicate an additional contribution of the Co redox process on the overall discharge capacity of the electrode cycled until – 0.70 V. Results also show that there is an increase on the cycle life of the Co coated alloy cycled until the cut-off potential of – 0.80 V, but there is a raise on the degradation processes for electrodes cycled until – 0.70 V.

Figure 2 presents representative *ex situ* XANES results in the transmission mode at the Co K-edge for electrodes cycled 100 times. Comparing the XANES for the samples with that for Co_3O_4, it is concluded that a major oxidation of Co takes place on the material cycled until – 0.7 V, while for the alloy cycled until – 0.8 V the cobalt layer retains the metallic structure. These results can explain the major capacity loss of the electrodes cycled until more anodic potentials.

The Fourier Transform of the EXAFS signals for Co layer under *ex situ* and *in situ* charged conditions present essentially the same radial distribution (RD) as pure Co, indicating that the local structure surrounding the Co atoms must be similar. The magnitude of RD for the Co plated layer is smaller than that of the reference sample, suggesting that the coordination number is smaller in the former, as usually seen for rough materials.

The study of the Co environment on the Co electroless plated layer by EXAFS shows that there is no significant change in the cobalt environment with the alloy charging. The charged electrode showed higher coordination numbers in comparison to the *ex situ* sample, indicating the presence of more reduced and ordered Co clusters. The measured bond distances for the *ex situ* and the charged sample are similar to that of the Co standard, in agreement to the fact that the Co layer does not contribute to the hydrogen storage.

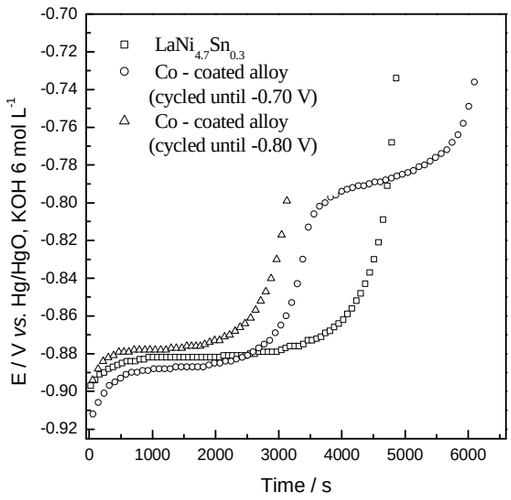

Figure 1 – Discharge profiles for the $LaNi_{4.7}Sn_{0.3}$ alloy electrode with and without the surface treatment, cycled at – 0.7 and – 0.8 V vs. Hg/HgO, KOH 6 mol L^{-1}.

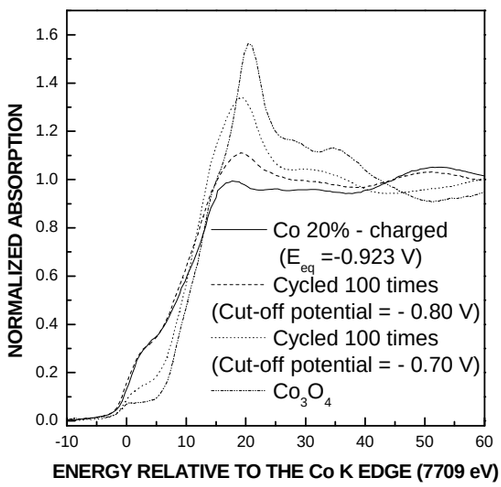

Figure 2 – XANES spectra at the Co K-edge for the $LaNi_{4.7}Sn_{0.3}$/20%Co alloy electrodes cycled using the two cut-off potentials (– 0.70 V and – 0.80 V vs. Hg/HgO, KOH 6.0 mol L^{-1}). The Co_3O_4 XANES spectrum is shown for comparison.

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