Effect of cobalt on physicochemical properties of AB_5-type metal hydride alloys

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This work reports the results of a systematic investigation on the effect of Co as substituent for Ni on several physicochemical properties of $LaNi_{(4.7-x)}Sn_{0.3}Co_x$ metal hydride alloys, where $0 \le x \le 0.7$. Electrochemical studies included measurements of charge/discharge polarization characteristics, the cycle life, and charge/discharge reaction kinetics at several states of charge and temperatures. Kinetic studies of the hydriding-dehydriding processes have been made using electrochemical impedance spectroscopy. The hydrogen equilibrium pressure were monitored as a function of the state of charge on activated electrodes. X-ray absorption spectroscopy has been used to study the electronic properties of La, Co and Ni in the alloys, and X-ray diffraction to obtain the unit cell lattice parameters.

The metal hydride alloys were prepared from high purity (>99.9%) starting materials by the arc melting technique under inert gas. X-ray diffraction (XRD) patterns were obtained for each alloy. Alloy powders with a mean particle size less than 10 μm crushed by a mechanical method were used. Electrodes were prepared by pressing a mixture comprised of 0.050 g of the alloy powder, 0.050 g of carbon black (Vulcan XC-72), and 33 weight percent (wt.%) polytetrafluoroethylene (PTFE) binder, on both sides of a nickel screen with a geometric area of 2 cm^2. Electrochemical measurements were done in a three-electrode cell in 6 mol L^{-1} KOH, with a Pt mesh counter electrode and a Hg/HgO-KOH 6 M reference electrode. Kinetic impedance measurements were made when the electrode charging capacity had reached the maximum, at open-circuit potential, on several states of charge and temperatures. The electronic properties of the alloys were studied by X-ray absorption spectroscopic (XAS) at the LNLS - National Synchrotron Light Source - Brazil.

X-ray diffractometry results indicate that all alloys present hexagonal $CaCu_5$-type structure. With the introduction of Co, the diffraction peaks shift to smaller angles, implying in an increase in the lattice parameters. Figure 1 shows XANES spectra at Ni K-edge for some of the studied alloys. It is observed that the magnitude of the pre-edge is not considerably affected due to the presence Sn and/or Co. This means that substitutions of Ni for Sn and/or Co do not lead to any appreciable change in the occupancy of the Ni 3d and/or 4p electronic energy states.

Figure 2 shows electrochemical impedance spectra for the activated $LaNi_{4.0}Sn_{0.3}Co_{0.7}$ alloy, obtained at several temperatures for a fully charged electrode. In the high-frequency range the impedance spectra show an arc with the magnitude and characteristic frequency essentially independent on the temperature and state of charge. In the lower frequency region, another arc is developed but here the features are strongly dependent on the temperature, state of charge of the electrode, and alloy composition.

Generally, it is seen that the presence of cobalt causes a decrease on the hydrogen equilibrium pressure and on the rate of capacity decay, and an increase in the cycle life and on the alloy activation time. All these phenomena could be related with the increase of the unit cell volume due to the presence of Co, as seen from the XRD measurements. The low frequency impedance features of the metal hydride electrodes were related to the charge transfer step of the hydriding-dehydriding processes [1]. It was found that the catalytic activity with respect to the hydrogen oxidation reaction is essentially independent on the Co content. This result was explained by a similar filling of the Ni 3d-band, as characterized from the XANES experiments.

Acknowledgements

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References

1. E. A. Ticianelli, S. Mukerjee, J. McBreen, G. D. Adzic, J. R. Johnson, and J. J. Reilly, J. Electrochem. Soc. 146 (1999) 3582.

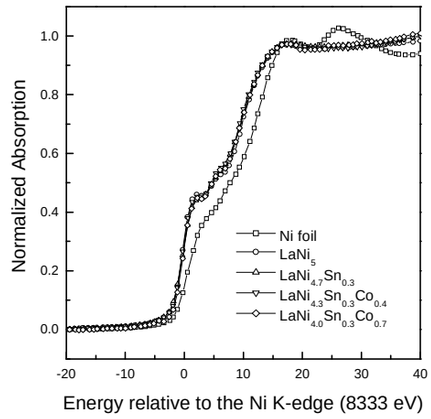

Fig. 1: XANES spectra in the transmission mode, at Ni K-edge for uncycled electrodes $LaNi_5$, $LaNi_{4.7}Sn_{0.3}$, $LaNi_{4.3}Sn_{0.3}Co_{0.4}$ and $LaNi_{4.0}Sn_{0.3}Co_{0.7}$.

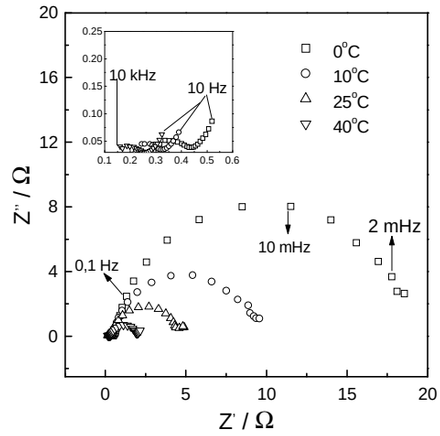

Fig. 2: Nyquist plots at several temperatures of $LaNi_{4.0}Sn_{0.3}Co_{0.7}$ fully charged electrode. The inset shows the arc in the high frequency range.