CHEMISTRY LETTERS, pp. 965-966, 1981.

HYDROGEN EVOLUTION AT $LaNi_5$ AND $MmNi_5$ ELECTRODES IN ALKALINE SOLUTIONS

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Both $LaNi_5$ and $MmNi_5$ electrodes were prepared and their cathodic polarization characteristics in alkaline solutions were studied. As a result, they were found to have the high electrocatalytic activity for hydrogen evolution, almost comparable to Pt and Pd electrodes.

Since $LaNi_5$ was first proposed as one of the candidates for hydrogen storage materials[1], both fundamental and practical works have been published[2]. However, there seem to have been only a few publications on its electrochemical properties. Miles[3] has briefly reported the hydrogen overpotential of a $LaNi_5$ electrode in 30 % KOH at 80 °C being -1.25 V vs. SCE at 2 mA cm^{-2} with a potential sweep rate of 2 V min^{-1}. In this work, $LaNi_5$ and $MmNi_5$ (Mm: mischmetal) electrodes were prepared and their cathodic polarization characteristics in alkaline solutions were studied, together with the alloy-constituent metal electrodes.

The test electrodes were prepared by melting the stoichiometric mixtures of La, Mm, and Ni in an arc melting furnace under an argon atmosphere. Resulting alloy ingots were cut with a diamond blade, polished mechanically with fine emery papers and then mounted into glass holders with epoxy resin.

The cathodic polarisation characteristics were galvanostatically measured in 1 M KOH solution at 30 °C. The solution was agitated by bubbling H_2 gas during the measurement. Typical polarization curves are shown in Fig. 1. The $LaNi_5$ and $MmNi_5$ electrodes show fairly lower overvoltages than the La, Mm, and Ni electrodes. The logarithmic current densities, $\log(i_o/A\ cm^{-2})$, obtained by extrapolating the linear portion of the Tafel lines to the hydrogen equilibrium potential (-0.926 V vs. Hg/HgO), are -3.5 for $LaNi_5$, -3.7 for $MmNi_5$ and -5.1 for Ni. In contrast to relatively high overpotentials of the La, Mm, and Ni electrodes, the $LaNi_5$ and $MmNi_5$ electrodes have shown very high activity for hydrogen evolution, almost comparable to Pt [$\log(i_o/A\ cm^{-2})=-3.0$] and Pd [$\log(i_o/A\ cm^{-2})=-3.9$] electrodes. Such a synergistic effect was reported for the hydrogen evolution reaction on NiAs, $NiTe_2$, and NiSi electrodes[4]. The synergistic effect of $LaNi_5$-type electrodes may also be attributed to the change of the electronic property caused by the 5d-electrons of La. $MmNi_5$ is presumably less active because of the presence of the 4f-electrons, which hinder the effect of the 5d-electrons. The reaction scheme of hydrogen evolution is supposed to be the same among the $LaNi_5$, $MmNi_5$, and Ni electrodes; i,e, the Volmer-Tafel process proposed for Ni electrode[5], since no pH dependence of the potential was observed for all these electrodes. Furthermore, the result of the X-ray diffractometry showed similar lattice parameters between the $LaNi_5$ and $MmNi_5$

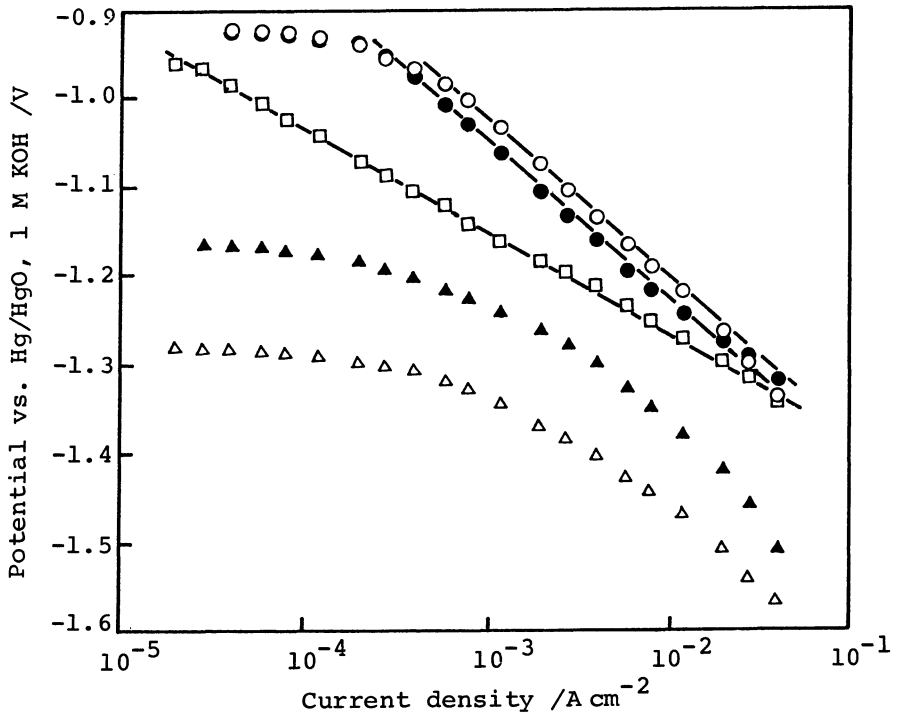

Fig. 1 Cathodic polarization curves in 1 M KOH at 30 °C

○:$LaNi_5$, ●:$MmNi_5$, □:Ni, △:La, ▲:Mm .

electrodes. This is in agreement with the view of Shamsul Huq and Rosenberg[4] that geometric factors in the most part may govern reaction mechanisms, whereas electronic factors may largely govern reaction kinetics. The steep Tafel slope of the $LaNi_5$ and $MmNi_5$ electrodes can be explained by assuming a moderate coverage, θ, of adsorbed hydrogen atoms[6].

The authors wish to thank Assoc. Prof. Dr. Hiroshi Nagai of Osaka University for his help in preparing alloys.

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(Received April 15, 1981)