THE KINETICS OF HYDROGEN TRANSPORT THROUGH AMORPHOUS Pd$_{82-y}$Ni$_y$Si$_{18}$ ALLOYS (y = 0 TO 32) BY ANALYSIS OF ANODIC CURRENT TRANSIENT

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Hydrogen transport through amorphous Pd$_{82-y}$Ni$_y$Si$_{18}$ alloys (y = 0 to 32) prepared by melt-spinning technique was investigated in 0.1 M NaOH solution by analysis of the anodic current transient. For this purpose, the anodic current transient was first measured as a function of the hydrogen discharging potential, in an attempt to establish the boundary condition at the electrode surface during hydrogen transport. According to the theoretical equation for the current transient derived under the boundary condition at the electrode surface during hydrogen extraction suggested in this work, kinetic quantities governing hydrogen extraction were then determined.

Fig. 1 shows the plot of (current × time$^{1/2}$) versus logarithm of time, obtained from the Ni-free Pd$_{82}$Si$_{18}$ electrode in 0.1 M NaOH solution by jumping the hydrogen pre-charging potential of −0.1 V(RHE) to the hydrogen discharging potential of 0.9 V(RHE). Fig. 1 does not exhibit any plateau region but rather an upward convex shape, which indicates the non-Cottrell behaviour of the anodic current transient [1]. Furthermore, all the anodic current transients measured at various hydrogen discharging potentials ranging from 0.5 to 0.9 V(RHE) were found to coincide very well with each other in shape as well as in value. From the good agreement between the anodic current transients theoretically calculated and experimentally measured, it is suggested that the change in surface concentration of hydrogen with time is uniquely given by the rate of hydrogen transfer from absorbed state at the electrode sub-surface to adsorbed state on the electrode surface. This means that neither the 'constraint of constant concentration' nor the 'constraint by Butler-Volmer behaviour' is effective at the electrode surface during hydrogen extraction [2].

On the basis of the theoretical current-time relation under the 'constraint by hydrogen transfer of absorbed state to adsorbed state', the hydrogen diffusivity was determined to have an almost constant value of about 10^{-8} cm^2 s^{-1}, irrespective of the Ni content and in the absence of Ni, as shown in Fig. 2. On the other hand, it is inferred that the rate constant of hydrogen transfer decreases markedly with increasing Ni content. From the appearance of the current peaks related to the phase transformations between Ni(OH)$_2$ and NiOOH in the cyclic voltammogram of the Ni-containing electrode in contrast to the Ni-free electrode, it is proposed that the Ni(OH)$_2$ layer on the electrode surface acts as the effective barrier to hydrogen extraction by reducing the rate constant of hydrogen transfer.
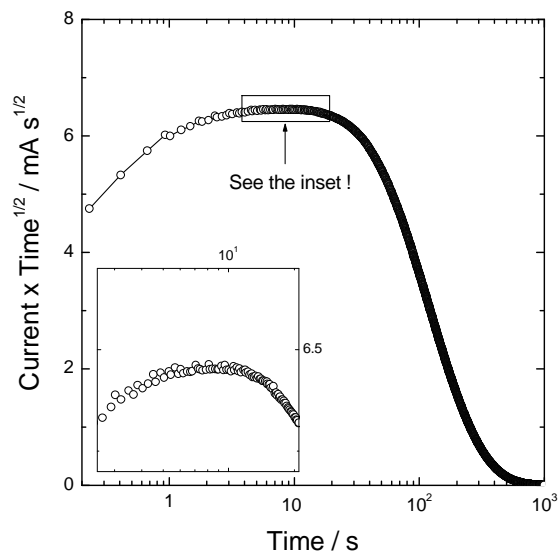

Fig. 1. Plot of (current × time$^{1/2}$) against logarithm of time, measured on the Ni-free Pd$_{82}$Si$_{18}$ electrode in 0.1 M NaOH solution by jumping the hydrogen pre-charging potential −0.1 V(RHE) to the hydrogen discharging potential 0.9 V(RHE).
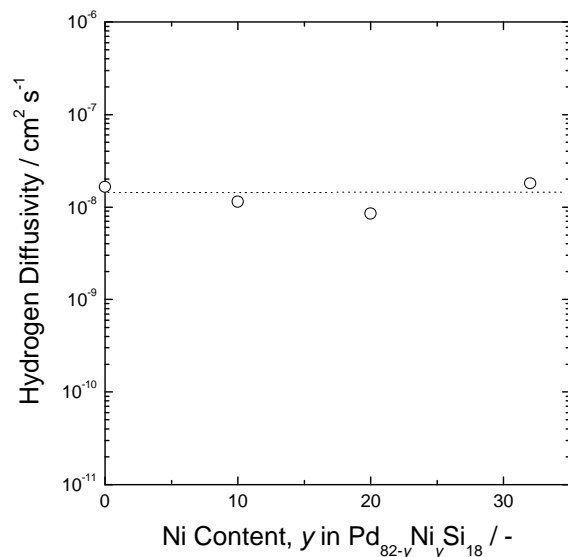

Fig. 2. Plot of the hydrogen diffusivity on a logarithmic scale versus the Ni content y in Pd$_{82-y}$Ni$_y$Si$_{18}$.

References
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