

Hydrogen diffusion in nanocrystalline palladium revealed by quasielastic neutron scattering

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Palladium hydride (PdH_x) is a prototypical metal hydride which has been studied extensively in both basic and industrial research fields for many decades. The remarkable properties are that palladium has a large absorption ability of hydrogen and the hydrogen atoms are highly mobile in the Pd lattice. For an H concentration higher than $x = 0.6$, the hydride crystal takes the β phase with an fcc (NaCl-type) structure and H atoms are accommodated at interstitial octahedral (O) sites (1/2, 1/2, 1/2) at ambient conditions. The diffusion dynamics of the H atoms has been studied by means of quasielastic neutron scattering (QENS) [1, 2]. The results suggest that the diffusion occurs through jumps between adjacent O-sites, though some of results are quantitatively conflict with each other. Our recent QENS works demonstrated that there exist two jump processes between the O-sites. From the temperature dependence of relaxation times and intensity, we conclude that the slow relaxation corresponds to the jump process between the ground states while the fast one is between the first excited states [3].

When the size of metal particles is reduced to a nanometer-scale, their physicochemical properties differ significantly from those in bulk and strongly depend on their size. In fact, it has been reported that there is a drastic change in the H₂ pressure-composition phase diagram for the PdH_x nanoparticles. In order to explore the diffusion dynamics in nanocrystalline PdH_x, QENS measurements were carried out by using a HFBS spectrometer with an energy resolution (E_{res}) of 0.8 μeV at NIST (USA) [4]. The sam-

ple used is high quality Pd nanocrystals which have a truncated cuboctahedron shape and are of narrow size distribution (8.0 ± 0.9 nm). The nanocrystals are covered by polyvinylpyrrolidone (PVP) to avoid the adhesion between the nanocrystals. This time, we have made further QENS measurements on TOFTOF with $E_{\text{res}} = 8 \mu\text{eV}$ at FRM-II (Germany).

Figure 1 shows the overall Arrhenius plot of the relaxation times for nanocrystalline PdH_{0.47} together with the data for bulk PdH_{0.73}. It is evident that a new fast diffusion process is present in the nanocrystalline sample in addition to the slow process which is nearly same as the one in bulk, i.e., the O-site jump process. Note that the new process differs from the fast relaxation observed in the bulk PdH_x. The fast process becomes more prominent at high temperatures, indicating that it comes from the hydrogen in a metastable site. The recent neutron diffraction work on PdD_x suggests that a part of subsurface hydrogen is accommodated at tetrahedral (T) sites (1/4, 1/4, 1/4) [5]. We infer that the fast process is the jump diffusion between the T-sites. Some strain and distortion effects near the surface can cause the strong modification of the potential energy of the interstitial sites. As a consequence, the T-sites are stabilized in the subsurface region.

References

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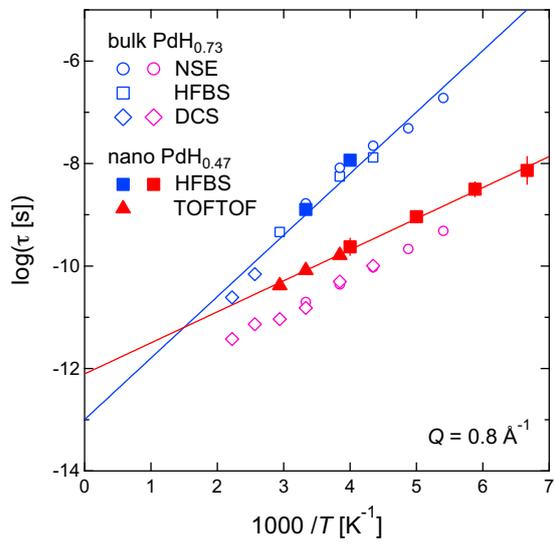


Fig. 1. Arrhenius plots of relaxation times for the hydrogen motions in nanocrystalline $PdH_{0.47}$ and bulk $PdH_{0.73}$.