

## Dynamics of hydrogen atoms in PdPt nanoparticles

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The nanometer-sized metals attract much attention since their physical and chemical properties are substantially different from those of bulk metals. Kobayashi et al. found that the phase-separated nanoparticles of Pd-core and Pt-shell are mixed to be solid solution alloy by repeating hydrogen absorption/desorption processes at 373 K [1]. Our neutron powder diffraction (NPD) measurements for solid solution Pd<sub>0.8</sub>Pt<sub>0.2</sub>D<sub>0.36</sub> nanoparticles revealed that D atoms are located at the interstitial octahedral (O) and tetrahedral (T) sites of an fcc lattice, as schematically shown in the inset of Fig. 1 [2]. Interestingly, 47% of D atoms occupy the T sites even at 300 K, which is larger than that for PdD<sub>0.36</sub> nanoparticles (31%). This means that the hydrogen absorption sites (T-sites) are more stabilized by the insertion of Pt atoms, although single Pt metal does not absorb hydrogen. In this study, we have investigated the diffusion dynamics of hydrogen atoms in solid solution Pd<sub>0.8</sub>Pt<sub>0.2</sub> nanoparticles by means of quasielastic neutron scattering (QENS).

The mean diameter of Pd<sub>0.8</sub>Pt<sub>0.2</sub> nanoparticles was determined to be 5.0 nm from TEM images. The nanoparticles are covered by protection polymer, polyvinylpyrrolidone (PVP), to avoid the adhesion between the nanoparticles. The total amount of sample with PVP was 766 mg. The hydrogenation was carried out at 100 kPa and 21°C for 1 day. The hydrogen concentration ( $x = 0.47$ ) was determined from the reduction in H<sub>2</sub> pressure of the gas handling system. The QENS experiments were performed on Pelican and Emu spectrometers at ACNS, ANSTO. Using these instruments, we have investigated the relaxation phenomena in time range from 1 ps to 5 ns.

Figure 1 shows the Arrhenius plot of

the relaxation times ( $\tau$ ) for Pd<sub>0.8</sub>Pt<sub>0.2</sub>H<sub>0.47</sub> nanoparticles obtained by Emu ( ) and Pelican ( ). We also plot the data for PdH<sub>0.47</sub> nanoparticles ( ) obtained in our previous QENS experiments [3]. There are two relaxation processes in both Pd<sub>0.8</sub>Pt<sub>0.2</sub>H<sub>0.47</sub> and PdH<sub>0.47</sub> nanoparticles. From our previous results [2,3], we assign the slow and fast relaxation processes to the hydrogen motions in the interior and subsurface regions of nanoparticle, respectively. In the slow relaxation process, the  $\tau$  and the activation energy of Pd<sub>0.8</sub>Pt<sub>0.2</sub>H<sub>0.47</sub> nanoparticles are smaller than those for PdH<sub>0.47</sub> nanoparticles. Interestingly, the fast relaxation time for Pd<sub>0.8</sub>Pt<sub>0.2</sub>H<sub>0.47</sub> nanoparticles is almost temperature independent below 250 K, suggesting tunneling processes. Thus, the substitution of Pt atoms in a Pd fcc lattice deforms the potential energy surfaces and enhances the diffusion of hydrogen atoms.

[1] H. Kobayashi et al., JACS 132, 5576 (2010).

[2] H. Akiba et al., JPCC 123, 9471 (2019).

[3] M. Kofu et al., PRB 94, 064303 (2016)

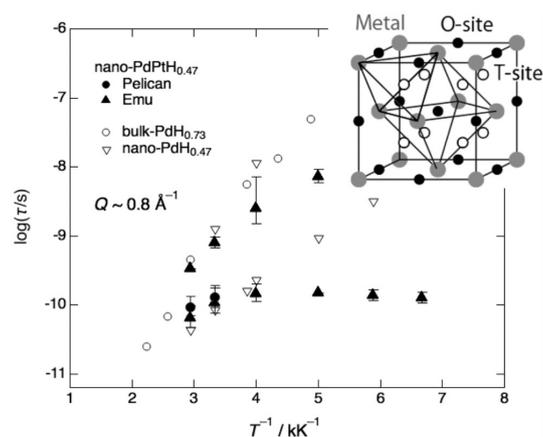


Fig. 1. Arrhenius plot of the relaxation times for Pd<sub>0.8</sub>Pt<sub>0.2</sub>H<sub>0.47</sub> and PdH<sub>0.47</sub> nanoparticles.