

Configurational and Communal Entropies in Non-stoichiometric PdH_x

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Non-stoichiometric palladium hydride (PdH_x) with vacancies for hydrogen exhibits a glass transition temperature (T_g), resulting in generation of both configurational and communal entropies. The communal entropy was evaluated under a given configurational entropy with a suitable hydrogen occupation of tetrahedral and octahedral sites of Pd using the standard molar entropy of formation ($\Delta_f S_{m(exp.)}$) calculated from the equilibrium pressures in pressure–composition–temperature (PCT) curves and the spectroscopic entropies of molecular hydrogen and PdH_x.

PCT curves with little hysteresis between hydrogenation and dehydrogenation processes were obtained just below the critical temperature T_c , at which the lattice volume mismatch between α and β phases of PdH_x is almost negligible. The $\Delta_f S_{m(exp.)}$ value calculated from the PCT curves was -83.4 ± 1.3 J/(K·mol_{H₂}) in the hydrogenation process and -87.3 ± 1.7 J/(K·mol_{H₂}) in the dehydrogenation process, showing only a relatively small discrepancy between the two.

Based on data from the literature, we assumed that the α phase, with its lower hydrogen concentration, was PdH_{0.006}, and that the β phase, with its higher hydrogen concentration, was PdH_{0.6} in the equilibrium hydrogenation reaction between α and β phases. We then estimated the difference in communal entropy (ΔS_{com}°) between PdH_{0.006} and PdH_{0.6} in terms of the $\Delta_f S_{m(exp.)}$ value, the hydrogen molar entropy (S_{m,H_2}°), the vibrational entropy (ΔS_{vib}°), the electronic entropy (ΔS_{ele}°), and given configurational entropy (ΔS_{conf}°). We found that near T_c , H atoms occupied both the octahedral and tetrahedral sites in PdH_{0.6}, with ΔS_{com}° approaching the value of the gas constant R (Fig.1). On the other hand, ΔS_{com}° approached 0 J/(K·mol_H) near the glass transition temperature T_g , with H atoms occupying only all the octahedral sites in PdH_{0.6} (Fig.2).

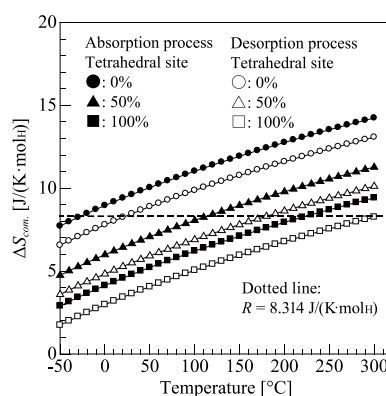


Fig. 1 Estimated communal entropy ΔS_{com}° for hydrogen absorption and desorption processes above -50 °C.

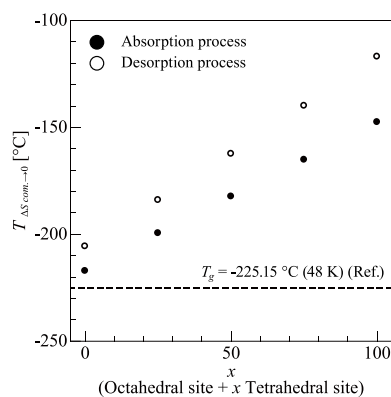


Fig.2 Relationship between temperature and the fraction of tetrahedral sites occupied (during full occupation of octahedral sites as communal entropy ΔS_{com}° approaches 0 J/(K·mol_H)).