Hydrogen evolution reaction following Slater-Pauling curve: Acceleration of rate processes induced from dipole interaction between proton and ferromagnetic catalysts

M. Morishita, Y. Okumura, R. Fukushima, H. Yamamoto, and H. Yanagita

Developing new concepts to design noble-metal-free catalysts is necessary to achieve the hydrogen economy and reduce global CO_2 emissions. Here, we provide novel insights into the design of catalysts with internal magnetic fields by investigating the relationship between the hydrogen evolution reaction (HER) and the Slater–Pauling rule. This rule states that adding an element to a metal reduces the alloy's saturation magnetization by an amount proportional to the number of valence electrons outside the d shell of the added element. We observed that rapid hydrogen evolution occurred when the magnetic moment of the catalyst was high, as predicted by the Slater–Pauling rule. Numerical simulation of the dipole interaction revealed a critical distance, r_C, at which the proton trajectory changes from a Brownian random walk to a close-approach orbit towards the ferromagnetic catalyst. The calculated r_C was proportional to the magnetic moment, consistent with the experimental data. Interestingly, r_C was proportional to the number of protons contributing to the HER and accurately reflected the migration length for the proton dissociation and hydration and the O–H bond length in water. The magnetic dipole interaction between the nuclear spin of the proton and the electronic spin of the magnetic catalyst is verified for the first time. The findings of this study will open a new direction in catalyst design aided by an internal magnetic field.

Thermodynamic and magnetic properties for $Dy_2Fe_{14}B$ determined by heat capacity measurement from very low to high temperatures and solution calorimetry

M. Morishita, T. Abe, H. Yamamoto, A. Nozaki, and S. Kimura

The thermodynamic and magnetic properties for $Dy_2Fe_{14}B$, a principal constituent of rare-earth magnets, were investigated as a function of temperature via calorimetric measurements. Its standard entropy, $\Delta^T_0 S^\circ_m$, was obtained from the molar heat capacity, $C^\circ_{p, m}$, at $2-850$ K using Debye-Einstein spin-wave functions. The standard enthalpy of formation, $\Delta_f H^\circ_m$, was determined by acid solution calorimetry to provide the standard Gibbs energy of formation $\Delta_f G^\circ_m(T)$ as a function of temperature. $\Delta_f G^\circ_m(T)$ is useful for Calphad phase diagram calculations. The magnetic moment was calculated by separating the spin and lattice vibration terms for $C^\circ_{p, m}$ via the Curie temperature of 594.1 K. The results agree with direct magnetization measurements and indicate that the Fe 3d magnetic moments magnetize $Dy_2Fe_{14}B$ by aligning by an exchange interaction between the Dy 4f and Dy 5d and Fe 3d moments in a second-order phase transition. These findings will contribute to the design of magnetic materials.

モリブデン酸ジルコニウムにおけるイオン配置と磁性の凍結解凍現象の発現

宮武竜也，森下政夫，山本宏明

エチレングリコールを溶媒に用いた非水溶液電解による熱電変換材料の作製

山本宏明