Morphology effect of nickel phosphide on hydrogen evolution reaction

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Abstract: The nano of micro sized Ni_2P particles (Ni_2P-N and Ni_2P-M) were synthesized by a ligand stabilization method and applied for hydrogen evolution reaction (HER). The HER reaction was conducted in 0.5 M H_2SO_4 aqueous solution at room temperature with a rotation speed of 1600 rpm at a scan rate of 5 mV s^{-1}. The Ni_2P catalyst was characterized by XRD and zetasizer. Overall, the HER overpotentials (η) measured for the nano and micro Ni_2P to produce cathodic current densities of 20mA/cm^2 were η = 214 mV and η = 450 mV, respectively.
Keywords: Nickel phosphide, hydrogen evolution reaction,

1. Introduction

Hydrogen is a candidate for a practical alternative energy source. Hydrogen evolution reaction (HER) occurs via a proton conducting polymer electrolyte membrane system with an electrocatalyst like Pt, which generates large current densities for the reaction at low overpotentials. Due to the high cost of Pt there have been many attempts to find the Pt replacements. The d-band electron density of Ni_2P (001) surface was calculated near the Fermi level [1-2]. It imply that Ni_2P (001) surface leads to a lower activation energy of hydrogen adsorption. Also Ni_2P is stable in an acidic solution because of the higher content of P atoms [3]. Although For the above reasons, Ni_2P is an active HER and stability relative to other electrocatalysts. Many researcher studied about HER mechanism of Nickel phosphide, shape effect, control Ni and P ratio, etc.[2-5] This study show Ni_2P electro property from a size.

2. Experimental (or Theoretical)

The nano-sized Ni_2P (Ni_2P-N) was synthesized by a ligand stabilization method using trioctylphosphine oxide (TOPO) as a coordinating agent. All synthesis conditions were carried out under nitrogen atmosphere using Schlenk line. The metal precursor Ni(acac)$_2$ was combined with trioctylphosphine oxide (coordinating ligand) in a 100 ml three neck flask with a condenser. The flask was placed on a heating jacket operated by a temperature controller. The mixture was degassed at 100 °C for 20 min to remove any moisture or oxygen. The temperature was set to heat to 320 °C, a TOP was injected, followed by heating for 4.5 h at 320 °C. The black product was washed with hexane and ethanol [3]. The micron-sized Ni_2P (Ni_2P-M) was prepared by thermal treatment of the Ni_2P-N at 450ºC for 1h in N_2.

Electrochemical measurements were conducted in three-electrode system: glassy carbon electrode (working), AgCl/3M KCl electrode (reference), and Pt (counter). The catalysts ink was prepared by mixing of 5 mg of catalyst, 41 μL of Nafion, 200 μL of IPA and 400μL of ethanol. After homogeneous solution was produced by sonication for several minutes, the catalyst ink was transferred to the working electrode and dried in room temperature until complete evaporation of solvent materials. The electrochemical data were obtained in 0.5 M H_2SO_4 at room temperature with a rotation speed of 1600 rpm at a scan rate of 5 mV s^{-1}. All potential were referred to reversible hydrogen electrode (RHE). The test was conducted under $-0.6\ V_{RHE} < E < 0\ V_{RHE}$.

3. Results and discussion

Figure 1 shows polarization profiles for HER over the Ni_2P catalysts. The Ni_2P-N exhibits a small onset potential of -79 mV versus RHE while Ni_2P-M shows much negative potential of -124mV, indicating a lower HER activation barrier for Ni_2P-N. Table 1compares onset potential, Tafel slope, and exchange current density for the catalysts. Tafel slopes for Pt/C, Ni_2P-N, and Ni_2P-M were 27.93, 66.97, and 154.93 $mVdec^{-1}$, respectively. Again, these results confirms a high HER activity of Ni_2P-N compared to Ni_2P-M.

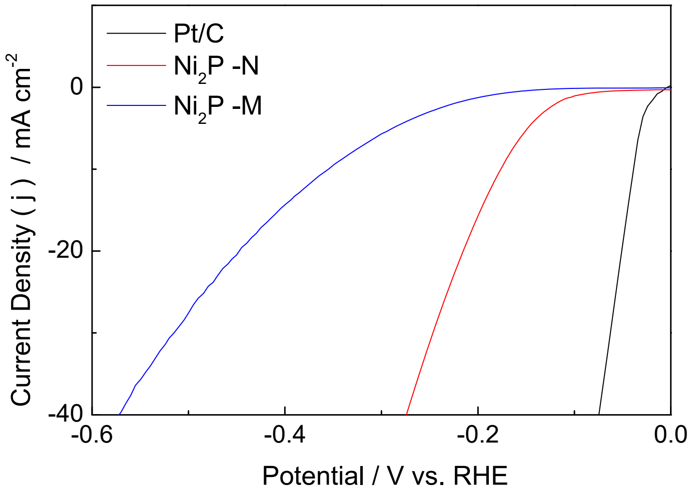

Figure 1. Polarization curves for HER

	Onset potential [mV]	Tafel slope [$mV\ dec^{-1}$]	Exchange current density [$mA\ cm^{-2}$]
Pt/C	0	27.93	0.325
Ni_2P-N (18 nm)	-79	66.97	0.033
Ni_2P-M (0.1μm)	-124	154.93	0.068

Table 1. Onset potential, tafel slope, and exchange current density of different catalysts

4. Conclusions

Two kind of Ni_2P catalysts with different sizes (Ni_2P-N and Ni_2P-M) were prepared to investigate the effect of particles size on the HER activity. The Ni_2P-N exhibited a smaller onset potential and Tafel slope than Ni_2P-M, demonstrating higher HER activity for the smaller Ni_2P catalysts.

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