



Metal-nitrogen intimacy of the nitrogen-doped ruthenium oxide for facilitating electrochemical hydrogen production

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ABSTRACT

In order to realize electrochemically efficient hydrogen production, various endeavors have been devoted to developing hydrogen evolution reaction (HER) electrocatalysts having zero hydrogen binding energy ($\Delta G_{H^*} = 0$) for balancing between adsorption and desorption. This work demonstrated that *nitrogen* doping improved the HER activity of ruthenium oxide by letting its ΔG_{H^*} approach zero or facilitating hydrogen desorption process. A highly nitrogen-doped ruthenium oxide catalyst guaranteeing the ruthenium-nitrogen intimacy was prepared by employing a polymer whose nitrogen-containing moiety (pyrrolidone) was *strongly* coordinated to ruthenium ion in the precursor solution prior to calcination. The less electronegative nature of nitrogen (when compared with oxygen) decreased the free energy uphill required for desorption of hydrogen intermediate species sitting on the nitrogen (H^*N to $1/2 H_2 + ^*N$) to make the desorption process more favored. Also, the nitrogen dopant facilitated OH⁻ desorption from its neighboring ruthenium site ($HO^*Ru + e^-$ to $HO^- + ^*Ru$) since the less electronegative nitrogen withdrew less electrons from the ruthenium site. The ruthenium-nitrogen intimacy of the catalyst more than doubled the electrocatalytic HER current from 33 mA cm^{-2} for an undoped RuO_2 to 79 mA cm^{-2} for the nitrogen-doped RuO_2 at -50 mV_{RHE} .

1. Introduction

Hydrogen economy has been considered to be alternative to the present carbon economy based on fossil fuels due to the environmental issues [1–4]. Hydrogen fuel benefits from its pollutant-free nature and high gravimetric energy density [5]. It sounds ridiculous that a dominant amount of hydrogen has been produced by reforming fossil fuels and therefore carbon dioxide is emitted from the hydrogen production. For holding the environmentally benign nature of hydrogen economy, it is desired to produce hydrogen from non-carbon resources [6]. Electrochemical water-splitting has been considered as a representative carbon-free hydrogen production process [7]. Efficient, stable and cost-effective electrocatalysts for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) have been developed for improving water electrolyzers [3,8].

The electrocatalytic HER activities of catalysts have been estimated by the Gibbs free energy of the adsorption of hydrogen atom on their

active sites of the catalysts (ΔG_{H^*}) [9–13]. The HER exchange current density (j_0) as a measure of the HER activity was maximized when the hydrogen adsorption and desorption were energetically and therefore kinetically balanced (i.e., $\Delta G_{H^*} = 0 \text{ eV}$). Platinum was a representative example of the nearby-zero- ΔG_{H^*} catalysts, showing high HER activity. The value of ΔG_{H^*} of Pt(111) was estimated to be about -0.29 eV [14]. The negative value of ΔG_{H^*} of Pt indicated that hydrogen adsorption was more favored than hydrogen desorption. To improve the HER catalytic activity of Pt, therefore, we should let the hydrogen surface species desorbed from its active site more easily. The ΔG_{H^*} moved in a positive direction closer to zero by employing ruthenium and its oxide favoring the desorption of the hydrogen surface species: ΔG_{H^*} (edge) = -0.36 eV for Pt to -0.33 eV for Ru; ΔG_{H^*} (terrace) = -0.29 eV for Pt (111) to -0.20 eV for Pt(111)Ru^{*} [14]. They were the easier-desorption catalysts, showing more excellent HER activities than Pt/C [15–18]. The NiTe nanorods as a support material even more improved the HER activity of RuO_2 by increasing the ΔG_{H^*} of RuO_2 from -0.31 eV to $+0.09$

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