

学 位 論 文 の 要 旨

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学位論文題目	Development of highly efficient electrocatalysts for fresh and seawater electrolysis under high current density (高電流密度下の淡水及び海水電解用高性能電極触媒の開発)		

学位論文要旨

Hydrogen production via electrochemical water splitting is a clean and secure technology. Water electrolysis consists of two main reactions, i.e., Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER). However, the sluggish OER kinetics and high-cost of commercial noble metal based catalysts such as Pt and RuO₂ based ones limit the practical application of this technology. Especially, to meet the practical industrial-scale requirements, the electrocatalysts should be operated at a high current density to achieve a high hydrogen production rate under long-term operation. Besides, using seawater directly to replace freshwater for the hydrogen production is attracting more and more attention for sustainable energy development because seawater is abundant. However, utilizing seawater based electrolyte remains great challenge due to the existence of competitive reactions between chlorine evolution reaction (CIER) and OER at the anode in the presence of Cl⁻ in the seawater, which always results in catalyst degradation and serious electrode erosion. In this dissertation study, the objective is to develop highly efficient electrode for water splitting with minimized operation cost, especially at a high current density even in a natural seawater based solution.

Firstly, CuVO_x nanobelt@NiO nanosheet is successfully synthesized using a facile one-step hydrothermal process combined with a calcination method. The obtained CuVO_x@NiO composite electrode exhibits remarkable HER activity in alkaline freshwater solution with an overpotential as low as 74 mV at 10 mAcm⁻², which also shows excellent stability and a fast kinetic reaction with a Tafel slope of 60.8 mVdec⁻¹. Moreover, it can maintain the potentials at difference constant current densities up to 300 mA cm⁻². Such a higher electrocatalytic performance could be attributed to the generation of real active (VO_x-Cu₂O) species during HER with increased O vacancies. Besides, lamellar NiO shell could also provide a large number of active sites and super-hydrophilic surface, which effectively facilitates the H₂O adsorption and decomposition to H_{ads} intermediates. It is found that the intrinsic reaction activity for the conversion of H_{ads} to H₂ could be improved by the VO_x-

Cu₂O core with rich O vacancy defects. This pioneer work provides a novel catalyst structure and superb properties for the HER in the alkaline electrolyzer.

Secondly, *in-situ* growing of FeNiS_x/NiFe(OH)_x on nickel foam (NF) is successfully realized using a facile corrosion engineering followed by a fast and mild sulfurization process. The obtained electrode requires only a low overpotential of 270 mV at a high current density of 100 mA cm⁻² in alkaline simulated seawater (1 M KOH+0.5 M NaCl) and maintains mechanical stability at an industrial-level current density of 1 A cm⁻² without catalyst corrosion. Density functional theory (DFT) calculations reveals that the FeNiS_x/NiFe(OH)_x has high oxygen evolution reaction (OER) against chlorine evolution reaction (CIER) since S substitution on O site can effectively decrease the free energy gap between *OH to *O, making OER more efficient. For overall seawater electrolysis using it as the bifunctional electrocatalyst, the electrolyzer only requires a low cell voltage of 1.60 V at 10 mA cm⁻² and can sustain stable at the industrial-level current density of 1 A/cm² with a cell voltage of 2.81 V for 100 h, achieving a high hydrogen productivity without the catalyst deterioration.

Lastly, a MnCo₂O₄ nanowire coated with NiFe-Layered Double Hydroxide (NiFe-LDH) layer (MnCo₂O₄@NiFe-LDH) composite electrocatalyst prepared by a simple two-step hydrothermal method is applied for the seawater electrolysis, which exhibits low overpotentials of 219 and 245 mV for OER at a high current density of 100 mA cm⁻² in alkaline simulated and natural seawaters, respectively. It is found that the NiFe-LDH layer on the MnCo₂O₄ nanowire can serve as Cl⁻ protective layer to hinder the CIER and anode erosion and simultaneously improve the active surface area and intrinsic properties of MnCo₂O₄ nanowires, allowing for faster kinetics. While, the high valence states of Mn³⁺, Co³⁺, Ni³⁺ and Fe³⁺ play a crucial role for OER. In addition, when it is used as the bifunctional electrocatalyst for the overall natural seawater splitting, the MnCo₂O₄@NiFe-LDH (-)||MnCo₂O₄@NiFe-LDH(+) pair in a two-electrode cell only requires a low voltage of 1.56 V@10 mA cm⁻² and simultaneously maintains excellent stability at a high current density of 100 mA cm⁻² for over 100 h. Such an electrocatalyst could be a promising candidate for practical seawater splitting.

注) 和文 2,000 字以内又は英文 800 語以内

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