様式第２号（第５条，第１１条関係）

「課程博士用」

学 位 論 文 の 要 旨

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学位論文題目	Development of High-performance Electrocatalysts for Hydrogen Production from Fresh and Seawater Splitting (淡水および海水電解による水素製造のための高性能電極触媒の開発)		

学位論文要旨

Direct electrolytic splitting of water for the production of pure hydrogen (H_2) is a promising technology that can help achieve carbon neutrality. Especially, recently, seawater electrolysis to replace freshwater electrolysis for the H_2 production becomes more and more attractive since the seawater occupies about 97% of water resource on the earth and a large amount of sustainable energy including ocean energy could be produced in the future. However, owing to the high concentration of chlorine ions (Cl^-) in seawater, the chlorine evolution reaction and/or hypochlorite generation reaction always compete with the oxygen evolution reaction (OER) at the anode, and simultaneously chloride corrosion occurs on both the anode and cathode. Thus, effective electrocatalysts with high selectivity toward the OER and excellent resistance to chloride corrosion should be developed. In this dissertation, I focus on the development of state-of-the-art electrocatalysts for water and seawater splitting, especially at a high current density even in the natural seawater-based electrolytes.

Firstly, non-noble metal-based electrocatalysts for hydrogen evolution reaction (HER) was developed. Herein, to achieve effective interface construction on the HER electrocatalysts, epitaxial growth of NiS on the surface of one-dimensional (1D) Ni_3S_2 nanowire on nickel foam (NF) was performed, in which a Ni_3S_2/NiS electrocatalyst with a heterojunction structure via a solid-state phase transformation was synthesized. Benefiting from the strong charge transfer at the Ni_3S_2/NiS heterojunction interface, it is found that the d-band center was downshifted compared to the single component (Ni_3S_2 or NiS), which effectively optimized the valence state and the H adsorption of Ni, thus improved the HER activity. The obtained Ni_3S_2@NiS-250/NF showed the robust HER catalytic performance with a low overpotential of 129 mV to deliver the current density of 10 mA cm^{-2} with a small Tafel slope (75.5 mV dec^{-1}) in 1 M KOH media. Moreover, it exhibited superior durability for at least 50 h. This work provides a novel strategy for designing nickel sulfide-based catalysts for HER with high performance.

Secondly, since the designing of cost-effective catalysts with high-activity and ultra-stability for HER is important in the scaling-up of water electrolysis process, a Zn-VO_x-Co two-dimensional (2D) nanosheet with well-integrated heterostructure was successfully

synthesized on carbon fiber paper (CFP) by a facile electrodeposition approach. Interestingly, the obtained nanosheets composed of amorphous VO_x-Co and Zn-Co crystalline phases with a heterostructure. Density functional theory (DFT) calculations reveled that the dual-doping of Zn and VO_x optimized the d-band center of Co and balanced the adsorption and desorption of H, which enhanced intrinsic electrocatalytic HER activity. As a result, by using the optimum catalyst, a current density of 10 mA cm^{-2} at an overpotential as low as 46 mV and long-term electrochemical stability over 36 h in 1 M KOH solution was achieved. This work opens a new avenue for designing electrocatalysts with unique crystalline-amorphous heterostructure by dual-doping to achieve tunable surface properties as well as d-band structure.

Lastly, since seawater splitting requires highly active and stable electrocatalysts to sustain electrolysis without chloride corrosion, especially for the anode, a novel boron (B) doped $MnFe_2O_4$ spinel-type electrocatalyst with a heterostructure was derived from MnFe-MOF-74 precursor and applied for seawater electrolysis. It is found that the introduction of B species can effectively optimize the electronic configuration of $MnFe_2O_4$, with the promoted electron transfer ability between neighboring O to Fe_{Oh}, thereby significantly reducing the energy barrier of the electron transfer and boosting the reaction process. As expected, in the real seawater environment, it required a low overpotential of 330 mV for OER to drive a current density of 100 mA cm^{-2} at 60 ℃, and high stability for over 200-h continuing test without producing hypochlorite and corrosion. This work provides a new strategy for enhancing the intrinsic activity of spinel-type oxides in seawater splitting.

In conclusion, three state-of-the-art electrocatalysts have been successfully obtained for the freshwater and seawater electrolysis. The catalytic mechanisms have been explored in details. It is expected to provide promising low-cost electrocatalysts for the hydrogen production from water especially seawater electrolysis, and give the guidance for the design of effective electrocatalysts.